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AFRPL-TR-70-20

**INVESTIGATION AND COMPILATION
OF THE THERMODYNAMIC PROPERTIES OF
HIGH TEMPERATURE CHEMICAL SPECIES**

FINAL TECHNICAL REPORT AFRPL-TR-70-20

(1 JANUARY 1967 - 31 DECEMBER 1969)

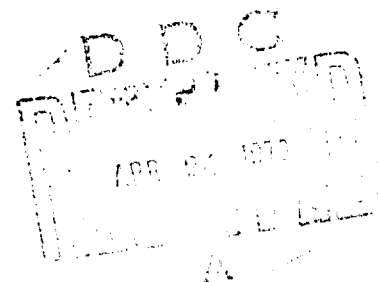
JANUARY 1970

**AIR FORCE ROCKET PROPULSION LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
EDWARDS AIR FORCE BASE, CALIFORNIA 93523**

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(Prepared under Contract Nr. F04611-67-C-0009
The Dow Chemical Company
Midland, Michigan 48640)



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(1 January 1967 to 31 December 1969)

INVESTIGATION AND COMPILATION OF THE THERMODYNAMIC
PROPERTIES OF HIGH TEMPERATURE CHEMICAL SPECIES

January 1970

Dow Report Nr. T0009-4Q-69

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AIR FORCE SYSTEMS COMMAND
RESEARCH AND TECHNOLOGY DIVISION
ROCKET PROPULSION LABORATORY
EDWARDS, CALIFORNIA
CONTRACT NR. FO4611-67-C-0009

THERMAL RESEARCH LABORATORY
THE DOW CHEMICAL COMPANY
MIDLAND, MICHIGAN 48640

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FOREWORD

This report was prepared by The Dow Chemical Company, Midland, Michigan, under USAF Contract FO4611-67-C-0009. The Contract was initiated under Air Force Project 3148, "Investigation and Compilation of the Thermodynamic Properties of High Temperature Chemical Species." The work was administered under the direction of the Rocket Propulsion Laboratory, Edwards Air Force Base, with Mr. Curtis C. Selph acting as Air Force Project Officer.

This is the final report, covering the work performed from January 1, 1967, through December 31, 1969. The Dow Report Number is T0009-4Q-69.

The following personnel of the Dow Thermal Research Laboratory were involved in this work: I. H. Carr, J. Chao, J. L. Curnutt, A. T. Hu, B. H. Justice, G. C. Karris, H. Prophet, G. C. Sinke, A. N. Syverud and D. U. Webb under the technical supervision of D. R. Stull and H. Prophet. During this period Dr. Chao and Dr. Justice terminated their employment with The Dow Chemical Company.

This technical report has been reviewed and is approved.

W. H. Ebelke, Colonel, USAF
Chief, Propellant Division

ABSTRACT

Supplements 25 through 32 of the JANAF Thermochemical Tables have been issued. These tables now contain 1,083 species, of which 117 new species were added and 243 tables were revised during this contract.

The final issue of the Propellant Ingredient Tables was made; it collected all previous series together in a single document.

The low temperature heat capacity of alpha-beryllium nitride has been measured; the entropy at 298°K is 8.157 gibbs/mol.

The infrared spectrum of $\text{Al}_2\text{Br}_6(\text{c})$ has been observed and the fundamental frequencies were assigned.

SECTION IINTRODUCTION

The research and development efforts in the area of chemical rocket propulsion need consistent, evaluated, thermodynamic properties for the combustion products. It was the objective of this program to provide these data as loose leaf sheets of tabulated properties of thermodynamic functions, available as the JANAF Thermochemical Tables. Since the temperatures of interest to rocketry range to several thousand degrees, the values have been tabulated from 0° to 6000°K. The tabulations cover heat capacity, enthalpy, entropy, free energy function, heat and free energy of formation and equilibrium constants of formation. The reverse side of the tabulation contains a write-up covering the data treatment and evaluation and a listing of the pertinent references. In this manner each species forms a completely self-contained unit on a single sheet.

In such a tabulation it is important to maintain proper consistency among the many interrelated measurements on the different species. A scheme is described which was implemented during this contract, to provide a computerized data base which summarized the effects of changes in one species on the properties of others.

A new simultaneous adjustment technique, for obtaining the most consistent set of values from many sets of interrelated reaction data, was used to analyze data pertaining to the heat of formation of HF(g) and several related fluorides. This application is treated in detail in Appendices A and B to this final report.

In many cases sufficient data are not available to produce reliable tabulations and so during this contract certain key measurements were made to fill such gaps. The low temperature heat capacity of a material provides the only reliable source of data on the entropy of solid compounds. Similarly the far infrared spectrum provides valuable information on the thermodynamically important vibrations of a molecule. These vibrational frequencies

are used to calculate the gaseous entropies with a high degree of confidence, when all the vibrations are measured. Experimental studies in these areas are reported, as part of this effort, for beryllium nitride and aluminum bromide.

SECTION IIJANAF THERMOCHEMICAL TABLESA. COMBUSTION PRODUCT TABLES

During this contract eight supplements to these Tables were issued, comprising numbers 25 through 32. A total of 360 Tables were issued, of which 117 were new issues and 243 were revised; the total number of Tables in the collection is 1,083. The elements cobalt, cesium and calcium were added during this contract, as were the oxides and chlorides of molybdenum and cesium and the fluorides of cesium and calcium. A large number of new ionized species and several new radicals were also added. Major groups revised during the contract period were fluoride species depending on HF, and the zirconium and titanium chlorides and fluorides. Tables I through VIII indicate the contents of the individual supplements 25 through 32.

The first applications of simultaneous adjustment to select heats of formation of interrelated species have been made for HF(g) , NaF(c) , $\text{BF}_3(\text{g})$, $\text{WF}_3(\text{g})$, $\text{CF}_4(\text{g})$, $\text{C}_2\text{F}_4(\text{g})$, $\text{CF}_3(\text{g})$, $\text{CBrF}_3(\text{g})$, $\text{CClF}_3(\text{g})$, $\text{CF}_3\text{I(g)}$, $\text{CHF}_3(\text{g})$, $\text{CF}_3\text{CN(g)}$, and $\text{C}_2\text{F}_6(\text{g})$. Details of the analyses are presented in Appendices A and B.

In the first year of this contract, a system was set up to keep track of the heats and entropies that went into the heat of formation of each table issued, which we term interrelations. In addition, the system produced from these interrelations a listing of all compounds which were dependent on a given heat of formation, which we term dependencies.

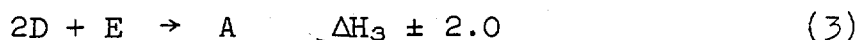
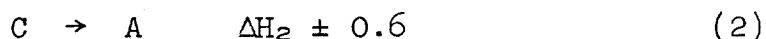
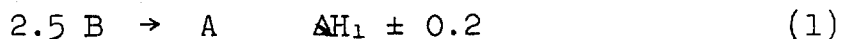
The complete system was operational during 1967 and was composed of the following components:

1. Input

The information relative to the determination of the heat of formation for a given compound (A) in the JANAF Tables is entered

on standard IBM cards. One card is used for each compound (B) that is involved in the heat of formation of A. The four numbers on the card are JANAF code numbers for B, JANAF code number for A, ΔH effect, and ΔS effect. As an example of the determination of the ΔH and ΔS effects, consider that the heat of formation of A is determined from the following equilibria: $2.5 B \rightleftharpoons A$, temperature range 1200-1600°K. The input card for this would be as follows: Code B, Code A, 2.5, 3.5. In this case, the ΔH effect is simply the B coefficient, and the ΔS effect is B coefficient multiplied by the mean temperature.

If several reactions were averaged to obtain a heat of formation, then the ΔH effect becomes B coefficient multiplied by smallest error, divided by error in given reaction. As an example, consider the reactions:



The input cards would be as follows:

Code B, Code A, 2.5, 0,
 Code C, Code A, 0.33, 0,
 Code D, Code A, 0.2, 0,
 Code E, Code A, 0.1, 0,

The cards are ordered by code number A and then input to deck 3413/HP, which produces two tapes. One tape contains the information in the same order as the cards. This is INTERNC. The other has the information alphabetized on code number A. This is ANTERNC.

2. Sorting

INTERNC is used as input to deck 3412/HP, which then sorts the information on Code B into alphabetic order and in decreasing effect of ΔH and ΔS . This is then written onto the DEPENDC tape.

3. Printing

ANTERNL is then input to deck 3152/HP, which looks up the code numbers on either FORMNAM or XFORMAM disk files. FORMNAM contains the formula, state, name, heat of formation and uncertainty of each compound in the JANAF Tables, while XFORMAM contains the same information for auxiliary compounds not in the Tables. This information is then printed out and is the Interrelationship Listing.

DEPENDC is used as input to deck 3342/HP, which prints out the same information as deck 3152/HP in a similar manner. This printout is the DEPENDENCY listing.

4. Updating

The information on the FORMNAM and XFORMAM disk files can be updated, using deck 3411/HP.

Examples of the two listings are shown in Tables IX and X.

B. PROPELLANT INGREDIENT TABLES

The previously issued loose leaf Series A through E and a new Series F have been combined together in a single report, AFRPL-TR-67-311, December 1967. The heat of formation and density data are tabulated in Brutto order and the write-ups of each compound are collected in a separate section. An index to the names and formulas completes the report. This Confidential publication constitutes the final report under this subsection of the JANAF Tables.

Table IJANAF Thermochemical Data

Supplement No. 25, Issued March 31, 1967

Title Page	Cl ₄ O ₂ (c)	*OTi(β)
AlN(g)	*Cl ₄ O ₂ (l)	OTi(l)
BeH ₂ O ₂ (g)	Cl ₄ O ₂ (g)	OTi(g)
BeO ₄ W(c)	FMg(g)	O ₂ Ti(rutile)
Be ₃ N ₂ (α)	FW(g)	O ₂ Ti(anatase)
Be ₃ N ₂ (l)	F ₄ O ₂ (c)	O ₂ Ti(l)
BrK(c)	F ₄ O ₂ (l)	O ₂ Ti(g)
BrK(l)	F ₄ O ₂ (g)	O ₃ Ti ₂ (c)
BrK(g)	F ₆ W(l)	O ₃ Ti ₂ (l)
Br ₂ K ₂ (g)	F ₆ W(g)	O ₅ Ti ₃ (α)
CSi(α)	H ₂ MgO ₂ (c)	*O ₅ Ti ₃ (β)
*CSi(β)	H ₂ O ₄ W(c)	*O ₅ Ti ₃ (l)
*CSi(g)	H ₂ O ₄ W(g)	Si(ref)
*CSi ₂ (g)	MgO ₄ W(c)	Si(l)
C ₂ H(g)	NSi(g)	Si(g)
*C ₂ N(g)	*NSi ₂ (g)	Si ₂ (g)
*C ₂ Si(g)	N ₄ Si ₃ (α)	Si ₃ (g)
Cl ₂ O ₂ W(c)	N ₅ P ₃ (c)	
Cl ₂ O ₂ W(g)	OTi(α)	

*New Table

Table IIJANAF Thermochemical Data

Supplement No. 26, Issued June 30, 1967

Title Page	HS(g)	Mg ₂ O ₄ Ti(l)
Al(l)	*H ₂ MgO ₂ (g)	*MoO(g)
AlBr ₃ (c)	*HgO(g)	*MoO ₂ (c)
AlBr ₃ (l)	IK(c)	*MoO ₃ (c)
AlBr ₃ (g)	IK(l)	*MoO ₃ (l)
Al ₂ Br ₆ (g)	IK(g)	*Na ₂ O ₄ W(c)
*BrW(g)	I ₂ K ₂ (g)	O ₂ Si(quartz)
Br ₅ W(c)	Li ₂ O ₃ Si(c)	*O ₂ Si(cristobalite, low)
Br ₅ W(l)	Li ₂ O ₃ Si(l)	*O ₂ Si(cristobalite, high)
Br ₅ W(g)	*Li ₂ O ₅ Si ₂ (c)	O ₂ Si(l)
Br ₆ W(c)	*Li ₂ O ₅ Si ₂ (l)	O ₃ Ti ₂ (c)
Br ₆ W(g)	MgO ₃ Ti(c)	O ₃ Ti ₂ (l)
*CBBr(g)	*MgO ₃ Ti(l)	RS(g)
*ClW(g)	MgO ₅ Ti ₂ (c)	Ti(g)
HMO(g)	MgO ₅ Ti ₂ (l)	
HP(g)	Mg ₂ O ₄ Ti(c)	

*New Table

Table IIIJANAF Thermochemical Data

Supplement No. 27, Issued September 30, 1967

Title Page	*Co(ref)	HLi(g)
Al ₂ O ₅ Si(sillimanite)	*Co(c)	Na ₂ O ₃ Si(c)
Al ₂ O ₅ Si(andalusite)	*Co(l)	Na ₂ O ₃ Si(l)
Al ₂ O ₅ Si(kyanite)	*Co(g)	Na ₂ O ₅ Si ₂ (c)
Al ₆ O ₁₃ Si ₂ (mullite)	*Co ⁺ (g)	Na ₂ O ₅ Si ₂ (l)
*C ₂ Cl ₄ (g)	F ₄ Ti(c)	OSi(g)
*C ₂ Cl ₆ (g)	F ₄ Ti(g)	O ₂ Si(g)
ClSi(g)	HLi(c)	
Cl ₄ Si(g)	HLi(l)	

*New Table

Table IVJANAF Thermochemical Data

Supplement No. 28, Issued December 31, 1967

Title Page	$\text{Cl}_4\text{Ti}(\text{g})$	$\text{Mg}_2\text{O}_4\text{Si}(\text{l})$
$\text{AlHO}(\text{g})$	$\text{FTi}(\text{g})$	$\text{NaO}(\text{g})$
$*\text{AlHO}^+(\text{g})$	$\text{F}_2\text{Ti}(\text{g})$	$*\text{NaO}^-(\text{g})$
$*\text{AlHO}^-(\text{g})$	$\text{F}_3\text{Ti}(\text{c})$	$*\text{Ti}^+(\text{g})$
$*\text{B}^+(\text{g})$	$\text{F}_3\text{Ti}(\text{g})$	$\text{Zr}(\text{ref})$
$\text{CCl}_3(\text{g})$	$\text{KO}(\text{g})$	$\text{Zr}(\alpha)$
$\text{CF}(\text{g})$	$*\text{KO}^-(\text{g})$	$*\text{Zr}(\beta)$
$\text{CH}(\text{g})$	$*\text{LiO}^-(\text{g})$	$\text{Zr}(\text{l})$
$\text{C}_2\text{F}_2(\text{g})$	$*\text{Mg}^+(\text{g})$	$\text{Zr}(\text{g})$
$*\text{C}_2\text{HF}(\text{g})$	$\text{MgO}_3\text{Si}(\text{c})$	$*\text{Zr}^+(\text{g})$
$\text{Cl}_4\text{Ti}(\text{c})$	$\text{MgO}_3\text{Si}(\text{l})$	
$\text{Cl}_4\text{Ti}(\text{l})$	$\text{Mg}_2\text{O}_4\text{Si}(\text{c})$	

*New Table

Table V

JANAF Thermochemical Data

Supplement No. 29, Issued June 30, 1968

Title	Page		
		BrTi(g)	*Cs(l)
*AlCl ⁺ (g)		Br ₂ Ti(c)	*Cs(g)
*AlCl ₂ ⁺ (g)		Br ₂ Ti(g)	*Cs ⁺ (g)
*AlCl ₂ ⁻ (g)		Br ₃ Ti(c)	*CsF(c)
*AlF ⁺ (g)		Br ₃ Ti(g)	*CsF(l)
*AlF ₂ ⁺ (g)		Br ₄ Ti(c)	*CsF(g)
*AlF ₂ ⁻ (g)		Br ₄ Ti(l)	*Cs ₂ (g)
*AlO ⁺ (g)		Br ₄ Ti(g)	*Cs ₂ F ₂ (g)
*AlO ₂ (g)		CTi(c)	F ₂ Si(g)
*AlO ₂ ⁻ (g)		CTi(l)	F ₂ Ti(g)
*Al ₂ O ⁺ (g)		C ₃ O ₂ (g)	F ₃ Ti(c)
*Al ₂ O ₂ ⁺ (g)		*ClCs(c)	F ₃ Ti(g)
*BCl ⁺ (g)		*ClCs(l)	*HMgO ⁺ (g)
*BCl ₂ ⁺ (g)		*ClCs(g)	ITi(g)
*BCl ₂ ⁻ (g)		*ClMg ⁺ (g)	*MoO ₂ (g)
*BF ₂ ⁺ (g)		ClTi(g)	*MoO ₃ (g)
*BF ₂ ⁻ (g)		*Cl ₂ Cs ₂ (g)	NTi(c)
*BHO ⁺ (g)		Cl ₂ Ti(c)	NTi(l)
BO(g)		Cl ₂ Ti(g)	Na ₂ O(c)
BO ₂ (g)		Cl ₃ Ti(c)	Na ₂ O(l)
*BO ₂ ⁻ (g)		Cl ₃ Ti(g)	Na ₂ O ₂ (c)
*BeCl ⁺ (g)		*Cs(ref)	
*BeHO ⁺ (g)		*Cs(c)	

*New Table

Table VI

JANAF Thermochemical Data

Supplement No. 30, Issued December 31, 1968

Title Page	*CaF ₂ (c)	FNa(c)
AlF ₃ Na ₃ (c)	*CaF ₂ (l)	FNa(l)
*AlF ₃ Na ₃ (l)	*CaF ₂ (g)	FNa(g)
AlHO ₂ (g)	ClTi(g)	*F ₂ K ⁻ (g)
AlO ₂ (g)	Cl ₂ Ti(c)	*F ₂ Li ⁻ (g)
AlO ₂ ⁻ (g)	Cl ₂ Ti(g)	F ₂ Li ₂ (g)
BCl ₂ ⁻ (g)	Cl ₃ Ti(g)	*F ₂ Na ⁻ (g)
BF ₂ ⁻ (g)	*Cl ₄ Mo(c)	F ₂ Na ₂ (g)
BO ₂ ⁻ (g)	*Cl ₄ Mo(l)	F ₂ Si(g)
CCl ₂ (g)	*Cl ₄ Mo(g)	F ₂ Ti(g)
CCl ₄ (g)	*Cl ₅ Mo(c)	F ₃ Li ₃ (g)
CHCl ₃ (g)	*Cl ₅ Mo(l)	ITi(g)
CH ₂ Cl ₂ (g)	*Cl ₅ Mo(g)	I ₂ Ti(c)
*C ₂ Cl ₂ (g)	*Cl ₆ Mo(c)	I ₂ Ti(g)
*C ₂ HCl(g)	*Cl ₆ Mo(g)	I ₃ Ti(c)
*Ca(ref)	*CsO(g)	I ₃ Ti(g)
*Ca(α)	*Cs ₂ O(g)	I ₄ Ti(c)
*Ca(β)	FH(g)	I ₄ Ti(l)
*Ca(l)	FLi(c)	I ₄ Ti(g)
*Ca(g)	FLi(l)	
*CaF(g)	FLi(g)	

*New Table

Table VIIJANAF Thermochemical Data

Supplement No. 31, Issued June 30, 1969

Title Page	CH ₂ (g)	F ₂ K ₂ (g)
AlF(g)	CH ₃ (g)	F ₂ Pb(c)
BF ₃ (g)	CIN(g)	F ₂ Pb(l)
*CBrF ₃ (g)	CN(g)	F ₂ Pb(g)
CBrN(g)	*CN ⁺ (g)	F ₂ Zr(c)
CClF ₃ (g)	*CN ⁻ (g)	F ₂ Zr(l)
CFN(g)	C ₂ F ₄ (g)	F ₂ Zr(g)
CF ₃ (g)	C ₂ F ₆ (g)	F ₃ N(g)
*CF ₃ I(g)	FK(c)	F ₃ Zr(c)
CF ₄ (g)	FK(l)	F ₃ Zr(g)
CHF ₃ (g)	FK(g)	F ₄ Zr(c)
CHN(g)	FZr(g)	F ₄ Zr(g)

*New Table

Table VIIIJANAF Thermochemical Data

Supplement No. 32, Issued December 31, 1969

Title Page	*C ₂ F ₃ N(g)	Cl ₄ Zr(g)
BF ₄ K(c)	C ₃ (g)	FSi(g)
*BF ₄ K(l)	C ₄ (g)	F ₂ O(g)
BF ₄ K(g)	C ₅ (g)	F ₂ Zr(g)
CCl(g)	ClZr(g)	F ₃ OP(g)
CCl ₃ (g)	Cl ₂ Mg(g)	F ₃ P(g)
CF ₂ O(g)	Cl ₂ Si(g)	F ₃ PS(g)
CF ₄ O(g)	Cl ₂ Zr(c)	F ₃ Si(g)
*CHCl(g)	Cl ₂ Zr(l)	F ₃ Zr(g)
*CHF(g)	Cl ₂ Zr(g)	F ₄ S(g)
CHN(g)	*Cl ₃ Si(g)	F ₅ I(g)
*CHP(g)	Cl ₃ Zr(c)	F ₅ P(g)
CH ₂ F ₂ (g)	Cl ₃ Zr(g)	F ₇ I(g)
C ₂ (g)	*Cl ₄ Mg ₂ (g)	HSi(g)
C ₂ ⁻ (g)	Cl ₄ Zr(c)	

*New Table

TABLE IX

B	A	COMPOUND NAME	DHF	H	U	S
-----	-----	-----	---	---	---	---
F H	(G)	HYDROGEN FLUORIDE	IS	-64.80	+-	0.3 KCAL/MOL
	C F ₄	(G) CARBON TETRAFLUORIDE		4.0		
	C ₂ F ₄	(G) TETRAFLUOROETHYLENE		4.0		
	F ₄ S	(G) SULFUR TETRAFLUORIDE		4.0		
	AL F ₆ NA ₃	(C) CRYOLITE		3.0		3.6
	F ₃ N	(G) NITROGEN TRIFLUORIDE		3.0		
	F ₂ FE	(C) IRON DIFLUORIDE		2.0		1.8
	F ₂ PB	(C) LEAD DIFLUORIDE		2.0		1.4
	CU F ₂	(C) COPPER DIFLUORIDE		2.0		1.1
	F ₃ FE	(C) IRON TRIFLUORIDE		1.0		0.7
	F ₂ H K	(C) POTASSIUM BIFLUORIDE		1.0		
	C F ₂	(G) CARBON DIFLUORIDE		0.4		

F K	(C)	POTASSIUM FLUORIDE	IS	-135.60	+-	0.3 KCAL/MOL
	C ₂ F ₆	(G) HEXAFLUOROETHANE		6.0		
	F ₂ H K	(C) POTASSIUM BIFLUORIDE		1.0		

F LI	(C)	LITHIUM FLUORIDE	IS	-146.50	+-	0.6 KCAL/MOL
	BE F ₄ LI ₂	(C) LITHIUM BERYLLIUM TETRAFLUORIDE		2.0		
	BE F ₃ LI	(C) LITHIUM BERYLLIUM TRIFLUORIDE		1.0		

F NA	(C)	SODIUM FLUORIDE	IS	-137.10	+-	0.3 KCAL/MOL
	C F ₄	(G) CARBON TETRAFLUORIDE		4.0		
	C ₂ F ₄	(G) TETRAFLUOROETHYLENE		4.0		
	F ₂ PB	(C) LEAD DIFLUORIDE		2.0		
	AL F ₆ NA ₃	(C) CRYOLITE		1.3		1.5

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TABLE X

A	B	COMPOUND NAME	DHF	H	U	S
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C F ₂	(G) CARBON DIFLUORIDE	IS	-41.00	+-	2.0	KCAL/MOL
C ₂ F ₄	(G) TETRAFLUOROETHYLENE			0.5		0.7
C H F ₃	(G) TRIFLUOROMETHANE			0.4		
F H	(G) HYDROGEN FLUORIDE			0.4		
C F ₄	(G) CARBON TETRAFLUORIDE			0.3		0.4
C H CL F ₂	(G) CHLORODIFLUOROMETHANE			0.3		
CL H	(G) HYDROGEN CHLORIDE			0.3		
H	(G) HYDROGEN, MONATOMIC			0.3		
F	(G) FLUORINE, MONATOMIC			0.3		

C F ₂ O	(G) CARBONYL FLUORIDE	IS	-151.70	+-	2.0	KCAL/MOL
F-	(A) FLUORIDE ION AQUEOUS			2.0		
H ₂ O	(L) WATER			1.0		
C O ₂	(G) CARBON DIOXIDE			0.8		0.4
C F ₄	(G) CARBON TETRAFLUORIDE			0.5		0.4

C F ₃	(G) CARBON TRIFLUORIDE	IS	-115.70	+-	2.0	KCAL/MOL
C H F ₃	(G) TRIFLUOROMETHANE			1.0		
H	(G) HYDROGEN, MONATOMIC			1.0		
C F ₄	(G) CARBON TETRAFLUORIDE			1.0		
F	(G) FLUORINE, MONATOMIC			1.0		

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SECTION III

THERMAL MEASUREMENTSA. LOW TEMPERATURE HEAT CAPACITY OF ALPHA-BERYLLIUM NITRIDE1. Experimental Procedure

The sample was used as supplied by the Brush Beryllium Company. It was checked, before the measurements, by X-ray diffraction (1) and found to be alpha-Be₃N₂. Analyses of the sample by Brush and Dow were in general agreement. The analysis accepted was 96.7% Be₃N₂ (by hydrolysis of the nitride to ammonia and titration), 2.7% BeO (neutron activation analysis for oxygen), 0.2% Be (quantitative hydrogen gas evolution in acid), 0.1% C (combustion to CO₂), and 0.3% Fe (weighted average of neutron activation and spectrographic analysis). The transfer and weighing of the sample into the calorimeter were done in a dry box. The sample mass used was 61.6975 g (corrected to vacuum); the molecular weight was taken as 55.0500.

Corrections to the individual heat capacity points were made by using literature values for the heat capacities of the observed impurities. For BeO the data of Gmelin (2) and K.K. Kelley (3) were joined smoothly. For Be, C, and Fe the smoothed data given in R. Hultgren et al. (4) were used. Approximating polynomials for each impurity were used to derive the corrections at each datum point. The correction to any single point was $3.5 \pm 0.5\%$ of the uncorrected heat capacities.

The apparatus is essentially that described by Oetting and McDonald (5). Since their work, the electrical circuits have been recalibrated. The system has been checked recently using benzoic acid as a standard and results are given in AFRPL-TR-66-175.

Three series of measurements were made on the sample; the data corrected for curvature are given in chronological order in Table XI. Temperature increments were used which approximated the smaller of the two quantities: (a) 10% of the absolute temperature, or (b) 10°K.

Table XI

Experimental Heat Capacity of α -Beryllium Nitride

<u>T</u> <u>°K</u>	<u>Cp</u> <u>gibbs/mol</u>	<u>T</u> <u>°K</u>	<u>Cp</u> <u>gibbs/mol</u>	<u>T</u> <u>°K</u>	<u>Cp</u> <u>gibbs/mol</u>
Series I		95.77	1.28	57.71	0.235
		104.73	1.67	63.57	0.336
156.18	5.00	114.10	2.18	70.08	0.443
165.39	5.71	122.88	2.71	77.21	0.602
174.92	6.46	131.04	3.24	85.22	0.886
183.97	7.24	139.90	3.86	93.97	1.21
192.63	7.86	149.43	4.52	103.22	1.61
201.61	8.59	158.38	5.21	112.63	2.11
211.54	9.37	166.87	5.85	121.57	2.63
221.72	10.16	174.96	6.47	129.87	3.18
241.49	11.62	182.71	7.10	138.26	3.75
251.75	12.31	190.17	7.72	146.78	4.37
261.69	13.02	197.37	8.25	154.82	4.95
271.36	13.63	204.77	8.85	162.48	5.54
280.76	14.27	213.75	9.57	169.79	6.10
289.94	14.85	223.80	10.34	176.82	6.62
298.92	15.43	244.51	11.85	183.59	7.21
307.70	15.89	254.66	12.57	190.14	7.73
		264.50	13.23	198.21	8.34
Series II		274.06	13.83	208.36	9.18
		283.38	14.46	218.73	9.97
25.29	0.006	292.49	15.07	238.28	11.45
28.11	0.017	301.40	15.58	248.15	12.11
30.90	0.020	310.11	16.09	258.29	12.83
33.91	0.043			268.13	13.49
37.26	0.050	Series III		277.70	14.10
40.97	0.064			287.04	14.68
44.97	0.129	26.69	0.012	296.17	15.29
49.43	0.156	29.16	0.016	305.10	15.78
54.25	0.203	32.02	0.022		
59.52	0.255	35.44	0.058		
65.32	0.359	39.12	0.076		
71.87	0.481	42.88	0.109		
79.12	0.667	47.12	0.130		
87.27	0.954	52.20	0.179		

The ice point was taken as 273.15°K and one defined calorie as 4.184 joules. The measurements of time, mass and electromotive force can all be traced to standards kept at the U. S. National Bureau of Standards.

2. Results

The smoothed values of the heat capacity and the corresponding thermodynamic functions are given in Table XII. Smoothing of the data was done using the least squares fitting of a polynomial. The scatter of the data was less than 1% from the smoothed line from 100°-310°K. At 75°K it was less than 0.05 gibbs/mol; thus the uncertainties below 100°K are considerably greater.

The measured heat capacity of α -Be₃N₂ varied from 1% of the total heat capacity observed at 25°K to 51% at 310°K. The entropy at 25°K was obtained using the Debye T³ relation. Measurements were made below 25°K, but were smaller than the errors associated with the apparatus in this temperature range.

B. THE FAR-INFRARED SPECTRA OF AlBr₃

1. Experimental Procedure

The far-infrared spectra of crystalline AlBr₃ were measured with the modified Beckman IR-11 spectrograph at the Chemical Physics Research Laboratory of The Dow Chemical Company. This instrument measures infrared spectra in the 35-600 cm⁻¹ region, with a resolution of approximately 3 cm⁻¹.

The sample and absorption cell were prepared in a dry box using a standard Nujol-mull technique (6). Reagent grade AlBr₃ was used. The absorption cell windows were made from polyethylene sheets 1 mm thick.

The spectra were measured within two hours after preparation of the absorption cell. Visual inspection of the cell following the measurements showed no signs of sample deterioration. The sample was left in the absorption cell and inspected periodically to determine the rate at which the AlBr₃ would decompose inside the cell. After a period of five days, most of the sample was dark

Table XII

Thermodynamic Functions for α -Beryllium Nitride

<u>T°K</u>	<u>C_p</u>	<u>S°_T</u>	<u>(H_T-H₀)/T</u>	<u>(G_T-H₀)/T</u>
25.00	0.0066	0.0022	0.0016	-0.0006
30.00	0.0192	0.0043	0.0033	-0.0010
35.00	0.0438	0.0090	0.0072	-0.0017
40.00	0.0754	0.0168	0.0137	-0.0031
45.00	0.1126	0.0278	0.0226	-0.0052
50.00	0.1563	0.0419	0.0337	-0.0081
60.00	0.2730	0.0800	0.0632	-0.0167
70.00	0.4473	0.1343	0.1048	-0.0294
80.00	0.6981	0.2094	0.1624	-0.0470
90.00	1.0354	0.3103	0.2399	-0.0704
100.00	1.4598	0.4406	0.3399	-0.1006
110.00	1.9651	0.6028	0.4641	-0.1387
120.00	2.5409	0.7980	0.6128	-0.1852
130.00	3.1755	1.0261	0.7851	-0.2409
140.00	3.8577	1.2861	0.9800	-0.3061
150.00	4.5778	1.5766	1.1957	-0.3810
160.00	5.3276	1.8959	1.4303	-0.4655
170.00	6.0999	2.2419	1.6822	-0.5597
180.00	6.8880	2.6128	1.9495	-0.6634
190.00	7.6847	3.0066	2.2303	-0.7762
200.00	8.4824	3.4210	2.5230	-0.8980
210.00	9.2730	3.8541	2.8257	-1.0284
220.00	10.0488	4.3034	3.1364	-1.1670
230.00	10.8033	4.7669	3.4534	-1.3134
240.00	11.5329	5.2421	3.7750	-1.4672
250.00	12.2370	5.7273	4.0995	-1.6278
260.00	12.9187	6.2206	4.4256	-1.7950
270.00	13.5834	6.7207	4.7525	-1.9681
280.00	14.2360	7.2265	5.0796	-2.1469
290.00	14.8766	7.7373	5.4064	-2.3308
300.00	15.4935	8.2521	5.7325	-2.5196
310.00	16.0554	8.7695	6.0566	-2.7129
298.15	15.3823	8.1566	5.6723	-2.4843

brown and another spectral measurement was made. Several bands were present which were not observed in the spectra of the fresh sample. All of the bands observed initially, however, exhibited lower absorbances, thus indicating that they can all be attributed to AlBr_3 .

2. Results

Ten absorption bands in the $40\text{-}600\text{ cm}^{-1}$ region were observed and measured. Figure 1 shows the absorption spectra of the fresh sample of AlBr_3 as originally prepared and after being thinned out mechanically.

Crystallographic studies indicate that crystalline AlBr_3 is dimeric (7). Raman studies of liquid AlBr_3 by Gerding and Smit (8) resulted in measurement of several frequencies, most of which were attributed to fundamental vibrational modes of dimeric AlBr_3 . A theoretical study of Al_2Br_6 (vapor) was presented by Miller (9) in which the eighteen fundamental vibrational frequencies were predicted, based on seven of the frequencies reported by Gerding and Smit (8).

The predictions of Miller are used to make tentative assignments for the bands which were observed. The measured frequencies and their tentative assignments are given in Table XIII.

Figure 1.
FAR-INFRARED SPECTRA OF ALUMINUM TRIBROMIDE

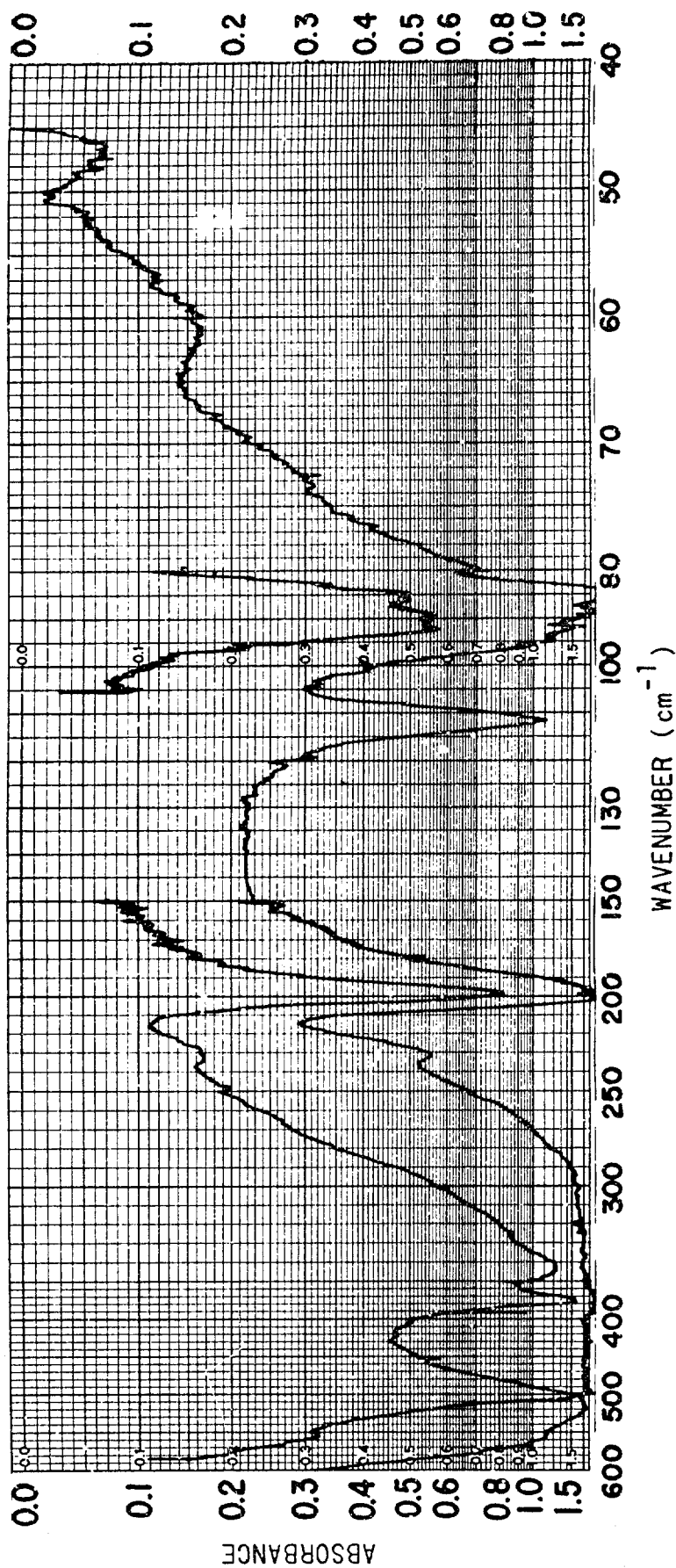


Table XIII

Observed Wavenumbers and Tentative Assignments for
Dimeric Aluminum Tribromide

<u>Wavenumber</u> <u>cm⁻¹</u>	<u>Tentative</u> <u>Assignment</u>
47	ν_5^*
61	$2\nu_{10}$
86	ν_{14}
91	ν_{18}
112	ν_9
198	ν_{17}
231	$\nu_{17} + \nu_{10}$
342	ν_{13}
377	ν_{16}
504	ν_8

*The vibrational mode ν_5 is not infrared active in the vapor phase, but is assumed to be perturbed by the lattice in such a way that it is active in the crystal phase.

C. REFERENCES

1. P. Eckerlin and A. Rabinau, Z. Anorg. Allgem. Chem., 304, 218 (1960).
2. E. Gmelin, Compt. Rend., 262, 1454 (1966).
3. K. K. Kelley, J. Chem. Phys., 11, 16 (1943).
4. R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley, "Selected Values of Thermodynamic Properties of Metals and Alloys," John Wiley & Sons, Inc., New York, 1963.
5. F. L. Oetting and R. A. McDonald, J. Phys. Chem., 67, 2737 (1963).
6. W. J. Potts, "Chemical Infrared Spectroscopy," John Wiley & Sons, Inc., New York, 1963.
7. K. N. Semenenko and T. N. Naumova, Russ. J. Inorg. Chem. (Engl. Transl.), 9, 718 (1964).
8. H. Gerding and E. Smit, Z. Physik. Chem., 51B, 217 (1942).
9. R. H. Miller, Jr., Ph.D. Thesis, Ohio University, 1965.

APPENDIX A

Simultaneous Adjustment of Thermochemical Data
Enthalpies of Formation of Hydrogen Fluoride
and Five Closely Related Fluorides

by

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INTRODUCTION

Recent research has provided much data pertinent to the values of ΔH_f° for HF(g) and HF(n H₂O). More accurate values for these quantities are desirable in themselves and because they are prime values on which many other fluorides are based. These quantities have remained relatively uncertain despite many calorimetric studies in the period from 1880 to 1950. Subsequent work emphasized important systematic errors, namely, various side reactions involving impurities, corrosion of containers and self-polymerization of HF(g).

The history of values selected from critical analyses (1,2,3) of the data may be summarized as follows:

Date and Reference	$\Delta H_f^\circ_{298.15}$, kcal/gfw		
	HF(g)	HF(50 H ₂ O)	HF(∞ H ₂ O)
1936 (1)	-64.0*	-75.56*	-78.2*
	-0.2	-0.10	-0.46
1952 (2)	-64.2	-75.66	-78.66
	-0.6	-0.66	-0.84
1965 (3)	-64.8 \pm 0.3	-76.316	-79.50
	-0.34	-0.46	-0.32
1968 (this selection)	-65.14 \pm 0.2	-76.78 \pm 0.1	-79.82 \pm 0.2

*Values correspond to 18°C rather than 25°C.

It is apparent from the differences tabulated between the lines that there has been a continual progression to more negative values. The present selections are no exception. The systematic trend in the values appears to be a reflection of increasing knowledge of the side reactions and increasing emphasis on minimizing them or correcting for them. Therefore, thorough analysis of the chemical reaction is essential for calorimetry involving hydrogen fluoride, fluorine, or, for that matter, almost any fluoride. This criterion is satisfied by several recent and pertinent calorimetric studies which make possible the selection of more reliable values for hydrogen fluoride.

Thermochemical data are normally used to select ΔH_f° values, one at a time, for a sequence of chemical species. This sequential adjustment of data has been the accepted method in thermochemistry for more than a century. Observations for HF are sufficiently numerous and complex to warrant a new approach, namely a simultaneous adjustment of ΔH_f° for several related species. Simultaneous adjustment may be generalized to include ΔG_f° and S° for those species having extensive measurements of ΔG_r° , ΔS_r° , and S° .

Guest et al. (60) recently applied a form of simultaneous adjustment to ΔH_f° for numerous species containing boron. Their work was published after completion of the present study (61).

This paper documents the simultaneous adjustments of ΔH_f° performed during preparation of new JANAF Thermochemical Tables for HF(g), NaF(c), BF₃(g), NF₃(g), and CF₄(g). Given first is a mathematical formulation for simultaneous adjustment. Pertinent thermochemical data for HF are reviewed, followed by the resulting simultaneous adjustments. These adjustments are discussed by analogy with those used in selection of the fundamental constants of physics and chemistry. Finally, some suggestions are offered for future experiments pertinent to HF.

Simultaneous Adjustment

In general, thermochemical observations exist for a series of reactions among several chemical species. It is assumed that the data from each observation may be reduced to a standard state value of $\Delta H_{298.15}^\circ$, or to $\Delta H_{298.15}$ if some states are nonstandard but well characterized. Reduction of the data also includes estimation of an overall uncertainty interval for ΔH° . Substitution of relatively well-known, fixed values of ΔH_f° (with their uncertainties) yields $R_{\underline{i}} + U_{\underline{i}}$, the observed value of some linear combination of unknowns, $\Delta H_{298.15}^\circ = F_{\underline{j}}$.

For a series of observations ($\underline{i}=1,2,\dots,\underline{m}$), $F_{\underline{j}}$ ($\underline{j}=1,2,\dots,\underline{n}$) is defined by \underline{m} heat-balance equations of the form:

$$\sum_{\underline{j}} c_{\underline{i}\underline{j}} F_{\underline{j}} = R_{\underline{i}} - E_{\underline{i}}, \quad [1]$$

where $E_{\underline{i}}$ is the error and $c_{\underline{i}\underline{j}}$ is the stoichiometric coefficient for unknown \underline{j} in observation \underline{i} . The stoichiometric coefficients are taken to be negative for reactants and positive for products. Values of $c_{\underline{i}\underline{j}}$ are presumed to be known exactly; they should correspond to exact balances of mass and charge.

Neither $F_{\underline{j}}$ nor $E_{\underline{i}}$ will ever be known exactly, but we wish to obtain adjusted values $F_{\underline{j}}'$ which are "best" approximations for $F_{\underline{j}}$. Deviations between the observations and these adjusted values are given by

$$E_{\underline{i}}' = R_{\underline{i}} - \sum_{\underline{j}} c_{\underline{i}\underline{j}} F_{\underline{j}}'. \quad [2]$$

Thus, the problem reduces to adjustment of an overdetermined set of observed values involving linear combinations of the unknowns.

The established procedure for adjustment of Equations [1] assumes that $E_{\underline{i}}' = 0$ for selected heats of reaction (or for a weighted average of selected values), and the heats of formation $F_{\underline{j}}'$ are obtained one at a time by use of Equations [2] in some sequential

fashion. Inconsistencies arising from multiple determinations or alternate paths are resolved in the selection process by attributing all (or most) of the deviations to those observations which are believed to be less accurate. This sequential selection of the variables will be called a sequential adjustment in order to distinguish it from the following alternative.

Simultaneous adjustments of Equations [1] are readily obtained by minimization of a suitable function of the weighted deviation E_i'/U_i . (Prerequisites for adjustment are $m > n$ and a nonsingular matrix of stoichiometric coefficients.) Two different minimization criteria appear useful: least squares, which minimizes the sum of squares of E_i'/U_i , and least sum, which minimizes the sum of absolute magnitudes of E_i'/U_i . Least squares and least sum correspond, respectively, to the L_2 -norm and the L_1 -norm of approximation theory (4). The so-called L_∞ -norm, which corresponds to minimization of the maximum value of E_i'/U_i , usually does not give acceptable adjustments (5) to Equations [1].

Least squares adjustments tend to distribute the deviations among all of the observations, while least sum adjustments assume at least as many zero deviations as there are variables (5). In the limit as simultaneous adjustment is reduced to stepwise selection of F_j' , least squares reduces to selection of the weighted average and least sum reduces to selection of the least uncertain observation.

Simultaneous adjustment may be extended to include the ΔG_f° and S° in the unknowns and ΔG_r° , ΔS_r° , and S° in the observations. Thermodynamics then requires for each chemical species the linear constraint:

$$\Delta H_f^\circ = \Delta G_f^\circ + 298.15 \Delta S_f^\circ, \quad (3)$$

where ΔS_f° is the entropy of formation of that species from the elements in their standard reference states. Linear constraints

may be incorporated (6) without changing the adjustment problem. This problem, i.e. the solution of linear systems of algebraic equations, is the subject of many algorithms (7,8,9) which have been programmed for digital computers. Least squares adjustments are obtained with these algorithms, but least sum adjustments are usually obtained by the methods of linear programming (10,11).

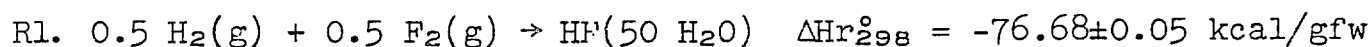
Selected Observations

The thermodynamic data considered for inclusion were those available at the end of 1968. Several reviews (12-16) were particularly helpful in screening the related fluorides for reliable and consistent links to HF. Data considered in the previous critical evaluations (1,2,3,17) were newly screened, based on current knowledge. This process led to the selection of five fluorides which appeared to be pertinent to the adjustment. These include NaF(c), BF₃(g), NF₃(g), CF₄(g), and C₂F₄(polymer).

The remainder of this section discusses the selected data. Since the selections are presumably neither definitive nor unique, suggestions of changes for use in future adjustments are welcome. There are several links, for example, which interrelate C₂F₆(g), C₂F₄(g), CHF₃(g), CClF₃(g), CBrF₃(g), and CF₃I(g) with the selected species. The inconsistencies for C₂F₄(g) and CHF₃(g) appear to be large enough so that these links will contribute little, if any, to a knowledge of HF. Thus, all of these species are subject to a secondary adjustment (see Appendix B).

The experimental data for each species are reduced to a chosen standard state for convenience in the subsequent analysis. One exception is HF(n H₂O) which is reduced to HF(50 H₂O). Other aqueous species in the ionized standard state of unit molality will hereafter be denoted by the description "(aq)." Data for aqueous species are reduced by means of the selected curves of Reference (17) whenever possible. Thermodynamic functions for

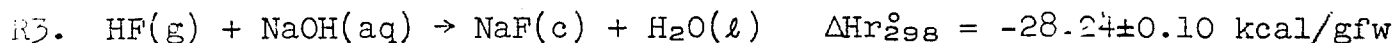
gaseous and condensed phases are taken from the JANAF Tables (18). Uncertainty intervals for calorimetric data are calculated from $2\bar{s}'_Q$, as recommended by Rossini (19), unless otherwise indicated. In some cases, the interval is increased by an additional contribution for the estimated systematic error. When the overall ΔH_r is the sum of two or more independent values, then the overall uncertainty interval is calculated by means of Equation 17 of Rossini (19). The twenty three selected reactions are discussed under the headings R1 through R23.



King and Armstrong (20) measured the heats of reaction of fluorine, oxygen and OF_2 with hydrogen by flame calorimetry at 30°C . The oxygen data agree with the accepted ΔH_f° for $\text{H}_2\text{O}(\text{l})$ and the fluorine data reduce to the value shown above. This is a very thorough study which serves well to illustrate the importance of side reactions such as corrosion. The later paper (20) increased the uncertainty to 0.09 kcal/gfw based on estimates of the systematic uncertainty. The smaller value of 0.05 kcal/gfw , exclusive of the systematic uncertainty, is used here to weight this observation more heavily.

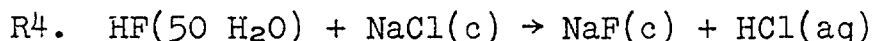


Johns and Barrow (21) obtained $D_e'' = 49310 \pm 100 \text{ cm}^{-1}$ from rotational predissociation of the vibrational levels in the UV spectra of HF. From this we derive $D_0'' = -135.067 \pm 0.3 \text{ kcal/gfw}$ and the corresponding value at 298.15°K .



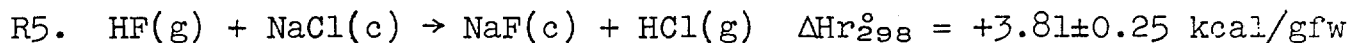
Rodenburg and Vanderzee (22) obtained values for the reaction $\text{HF}(\text{g}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaF}(\text{aq}) + \text{H}_2\text{O}(\text{l})$ from calorimetric studies with HF(real gas) at pressures of about 350 and 150 mm Hg. The

results are $\Delta H_r^\circ = -27.80 \pm 0.16$ and -28.01 ± 0.10 kcal/gfw, respectively, with preference being given to the latter value on experimental grounds (23). $\Delta H_r^\circ = -28.01 \pm 0.10$ kcal/gfw includes a non-ideality correction of approximately 0.20 ± 0.025 kcal/gfw. Combining this ΔH_r° with $-\Delta H_{\infty}^\circ \text{soln} = -0.23 \pm 0.01$ kcal/gfw (24) for NaF(c), we obtain the selected observation given above.



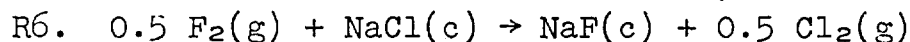
$$\Delta H_r^\circ_{298} = -2.41 \pm 0.07 \text{ kcal/gfw}$$

Coughlin (25) obtained $\Delta H_r^\circ = -1.53 \pm 0.06$ kcal/gfw at 30°C for $\text{NaCl(c)} + \text{HF}(5.716 \text{ H}_2\text{O}) \rightarrow \text{NaF(c)} + \text{HCl}(12.731 \text{ H}_2\text{O})$ from combination of five heat of solution measurements involving an acid solution of aluminum. Auxiliary data (17,18) yield a reduction to 25°C of 0.132 kcal/gfw, a reduction to $\text{HF}(50 \text{ H}_2\text{O})$ of 0.128 ± 0.03 kcal/gfw, and a reduction to HCl(aq) of -1.14 kcal/gfw.



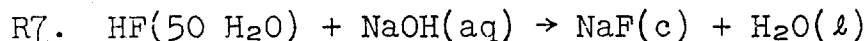
Hood and Woyski (26) reported equilibrium data for this reaction in the range $796\text{--}942^\circ\text{K}$. Second- and third-law analyses with the latest free energy functions (18) give $\Delta H_r^\circ = 5.91 \pm 0.11$ (second law) and 3.81 kcal/gfw (third law) at 298.15°K . The drift (difference between third- and second-law values of ΔS_r°) is -2.5 ± 0.1 eu, a rather precise value which is probably five times the overall uncertainty in the third-law ΔS_r° . This suggests a temperature-dependent error in the equilibrium constants, for example, an error in the analyses which determine the partial pressures, or a deviation of the condensed phases from their standard states. Attainment of equilibrium is confirmed by consistency of the K_p values, regardless of the direction of approach to equilibrium. Other aspects of the study appear to be thorough and well documented. It would be desirable to test for similar drifts in comparable studies (26) of $\text{BaCl}_2\text{--BaF}_2$ and $\text{NiCl}_2\text{--NiF}_2$, but this was not done because of uncertainties in the

free energy functions. Instead, it is noted that the third-law ΔH_r° is consistent with R3 within about 0.08 kcal/gfw, while the second-law value is clearly inconsistent. Such behavior is observed in systems where the equilibrium constants are essentially correct at one extreme in temperature, but show minor and increasing error toward the other extreme in temperature. Corrosion is suspected in this case, and the results at the lowest temperature should be the most reliable. The individual third-law values of ΔH_r° , ranging from 3.93 kcal/gfw at 796°K to 3.56 kcal/gfw at 942°K, yield a mean of 3.81 kcal/gfw, which is influenced by the preponderance of points at lower temperatures. This mean is adopted and the uncertainty interval is estimated as ± 0.25 kcal/gfw, which exceeds the range of the values and corresponds approximately to the maximum effect arising from uncertainty in the third-law ΔS_r° .



$$\Delta H_{r298}^\circ = -39.30 \pm 0.4 \text{ kcal/gfw}$$

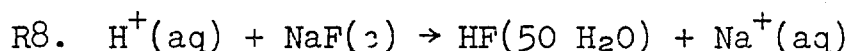
Calorimetric data for this reaction at 20°C were reported by von Wartenberg and Fitzner (27). The reduction to 25°C is insignificant. Although the study is old and incompletely documented by current standards, the results are consistent with recent work. An uncertainty of 0.4 kcal/gfw is assumed, based on 0.28 for the calorimetric experiments, and an estimate of 0.12 for other contributions.



$$\Delta H_{r298}^\circ = -16.57 \pm 0.05 \text{ kcal/gfw}$$

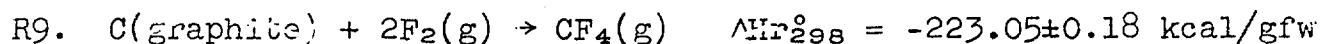
Kolesov and Skuratov (28) reported $\Delta H_n = -16.45 \pm 0.03$ kcal/gfw at 21.5°C for $\text{HF}(16 \text{ H}_2\text{O}) + \text{LiOH}(3800 \text{ H}_2\text{O}) \rightarrow \text{LiF}(3800 \text{ H}_2\text{O}) + \text{H}_2\text{O}(\text{l})$. It appears that this is the only modern determination of ΔH_n for HF with any alkali hydroxide. Auxiliary data (17,18) yield a reduction to 25°C of 0.074 ± 0.02 kcal/gfw, a reduction to

HF(50 H₂O) of 0.036 ± 0.01 kcal/gfw, and a combined reduction to LiOH(aq) and LiF(aq) of 0.001 kcal/gfw. The latter standard states may be considered as OH⁻(aq) and F⁻(aq), or as NaOH(aq) and NaF(aq), without affecting the $\Delta H_n = -16.34 \pm 0.05$ kcal/gfw. Combination of this value with $-\Delta H_{\infty}^{\circ} = -0.23 \pm 0.01$ kcal/gfw (24) for NaF(c) gives the selected ΔH_r° .

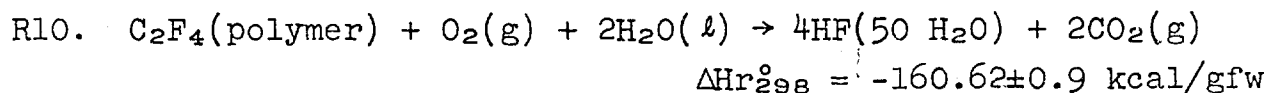


$$\Delta H_{r298}^{\circ} = 3.414 \pm 0.3 \text{ kcal/gfw}$$

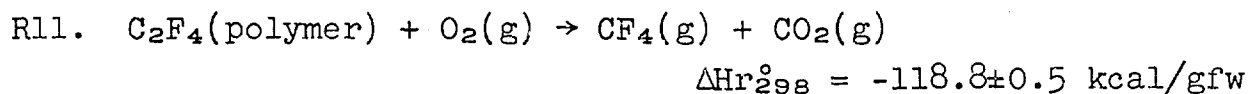
This "observation" is a combination of $\Phi_L = 3.184 \pm 0.3$ kcal/gfw (17) for HF(50 H₂O) and $\Delta H_{\infty}^{\circ} \text{ soln} = 0.23 \pm 0.01$ kcal/gfw (24) for NaF(c). It represents the composite of equilibrium and enthalpy data from which the dilution curve (17) was derived. Aqueous HF is a weak electrolyte which ionizes in dilute solutions according to the equilibria (a) $\text{HF} = \text{H}^+ + \text{F}^-$ and (b) $\text{HF} + \text{F}^- = \text{HF}_2^-$. The two ionization reactions make an overall contribution of about 3 kcal/gfw to Φ_L . Parker (17) used selected values of $\Delta H_a = -3.0$ and $\Delta H_b = +0.662$ kcal/gfw, along with concentrations based on selected equilibrium data, to calculate Φ_L in dilute solutions. Recent data suggest that minor changes in these calculations may be desirable. In particular, the calculated dilution curve shows increasing deviations at lower molalities when compared with the new measurements of Cox and Harrop (29). Agreement is satisfactory near HF(1100 H₂O), but near HF(6000 H₂O) the calculated heats of dilution are roughly 240 cal/gfw (or 32%) larger than the observed values. Alternative selections for K_a , K_b , ΔH_a and ΔH_b might reduce this discrepancy considerably. The equilibrium data, both new (30,30a,31) and old (17,24), are sufficiently divergent to allow changes in ΔH_a and ΔH_b of perhaps -0.2 and +0.5 kcal/gfw, respectively. Based on this review of the data, the uncertainty of Φ_L (50 H₂O) is estimated to be 0.3 kcal/gfw.



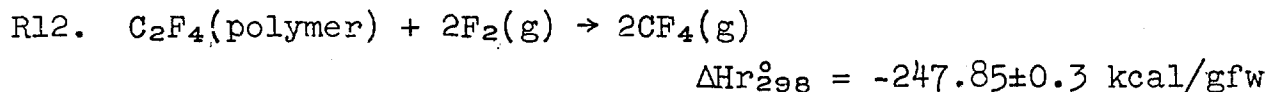
Greenberg and Hubbard (32) reported this result from a thorough study of the combustion in fluorine of natural and synthetic graphite.



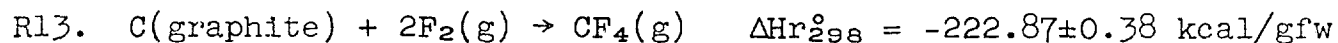
See the following discussion.



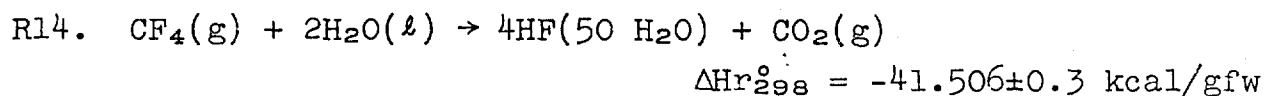
Good et al. (33) reported the calorimetric combustion of various Teflon-oil mixtures. Reactions R10 and R11 are derived by extrapolation from the observed product ratios of HF(10 H₂O)/CF₄ to the limits of only HF(10 H₂O) and only CF₄(g). R10 includes a reduction to HF(50 H₂O) of $-0.32 \pm 0.08 \text{ kcal/gfw}$.



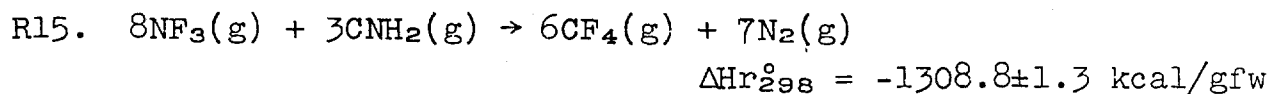
This ΔHr° appears to be a minor adjustment (12) of the earlier data of Domalski and Armstrong (13) who reported a value of $-247.92 \pm 0.07 \text{ kcal/gfw}$. The earlier value is labeled as Reaction R12a. Wood, Lagow and Margrave (34) reported -246.84 kcal/gfw for the same reaction. This is R12b and is reassigned an uncertainty of 0.2 kcal/gfw , since the authors' uncertainties and terminology are inconsistent with Rossini (19). The less negative value of R12b may be due to the fluorine used (34); possible causes are too low pressure (32) and presence of oxygen as an impurity (62). Effects due to phase transitions of C₂F₄(polymer) near 20 and 30°C might be involved, but the overall ΔHt for these transitions is only 0.2 kcal/gfw (35).



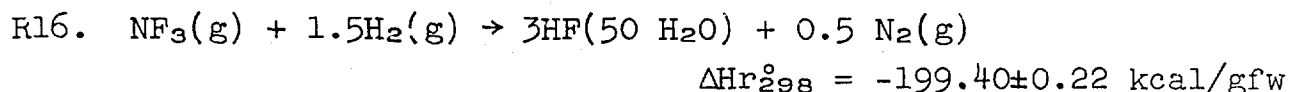
Domalski and Armstrong (13) reported this result from their combustions in fluorine of graphite-Teflon mixtures.



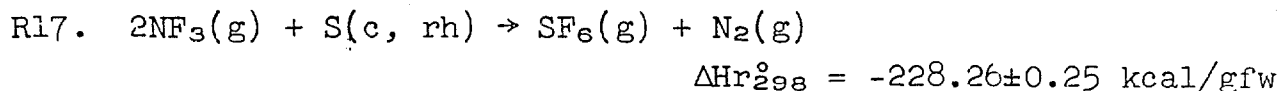
Cox, Gundry and Head (36) reported calorimetric combustions of mixtures of docosafluorobicyclohexyl ($\text{C}_{12}\text{F}_{22}$) with benzoic acid. This study, which is analogous to that of Good et al. (33) with Teflon-oil mixtures, yields two reactions having quite different product ratios of $\text{HF}(20 \text{ H}_2\text{O})/\text{CF}_4$. The above observation is obtained by taking the difference of these two reactions, dividing by 3.3, and adding a reduction to $\text{HF}(50 \text{ H}_2\text{O})$ of -0.12 ± 0.02 kcal.



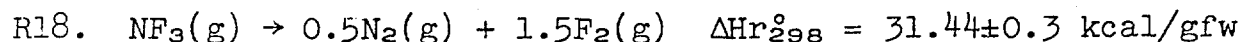
Walker (37) reported this calorimetric value at 298.15°K .



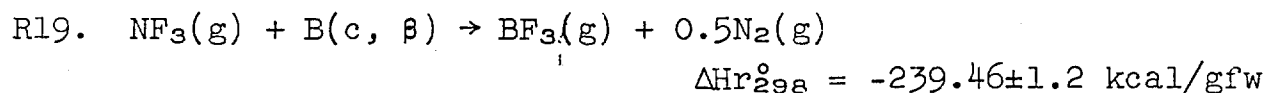
Sinke (38) reported a calorimetric value at 298.15°K of $\Delta\text{Hr}^\circ = -199.49 \pm 0.22$ kcal/gfw for a final state of $\text{HF}(123 \text{ H}_2\text{O})$. The reduction to $\text{HF}(50 \text{ H}_2\text{O})$ is $+0.09 \pm 0.01$ kcal/gfw.



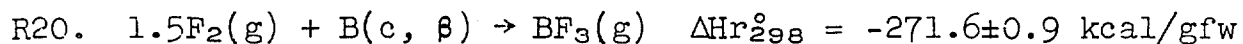
Walker (39) reported a calorimetric value at 298.15°K of $\Delta\text{Hr}^\circ = -228.26 \pm 0.2$ kcal/gfw. The uncertainty is reassigned as 0.25 kcal/gfw by reference to the original data, since the paper (39) is inconsistent in value and terminology with Rossini (19).



Sinke (40) reported calorimetric data for the explosion of mixtures of hydrogen with 10% excess of NF_3 and with 100% excess of NF_3 . The complex final states were not corrected to standard states; instead, the experiments were designed to minimize the corrections. The difference between the two sets of data yields the result above.

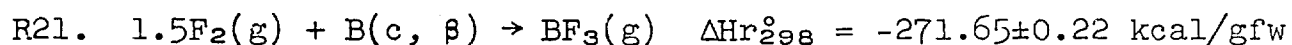


Ludwig and Cooper (41) reported a calorimetric value of $\Delta E_c^\circ/\text{M} = -22177 \text{ cal/g}$ after correction for 0.44% impurities in the sample of boron. Based on 10.811 for the atomic weight of boron, $\Delta E_c^\circ = -239.76 \pm 1.2$ and $\Delta\text{Hr}^\circ = -239.46 \pm 1.2 \text{ kcal/gfw}$. The amount of unburned boron remaining after combustion averaged 5% as determined by chemical analysis. This analysis was complicated by the retention on the bomb surfaces of some of the $\text{BF}_3(\text{g})$, apparently in the form of a metal fluoride - BF_3 adduct which was not identified. It is likely that the metal fluoride in the adduct was formed, at least in part, by corrosion. No correction was made for adduct formation, so the calorimetric result may be biased. Bias may also arise from the impurity correction (cf. R20); however, the existing bias appears to be much smaller than the assigned uncertainty.

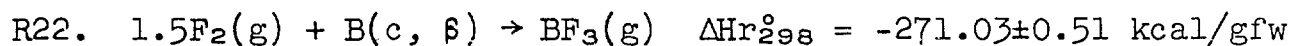


Wise et al. (43) reported the calorimetric result $\Delta\text{Hr}^\circ = -270.10 \pm 0.24 \text{ kcal/(10.82 g B)}$, based on correction for 0.62% impurities in the sample of boron. Reanalysis (42) of the sample with more reliable techniques showed the presence of 1.32% impurities. This made ΔHr° more negative by 1.5 kcal/gfw and increased the uncertainty by more than a factor of three. Here is a pointed example of bias caused by side reactions due to impurities.

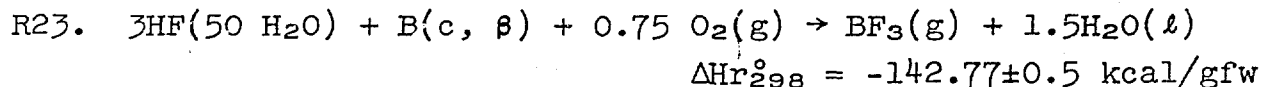
Calorimetric combustions in fluorine were also reported by Gross et al. (44). Their result was $\Delta H_r^\circ = -271.2 \pm 0.5$ kcal/gfw, including a correction of -0.6 kcal/mol for bias attributed to use of sulfur as an initiator for the reaction. The bias was estimated from data for fluorine combustions of α -boron and boron nitride with either sulfur or boron nitride as the initiator. This corrected result was not considered, since it came to our attention after completing the adjustment.



Johnson et al. (42) remeasured the heat of combustion in fluorine using two different experimental techniques with a zone-refined sample of boron. The sample contained 0.13% impurities (O, C, N and H), for which the corrections amounted to about 0.12% of ΔE_c° . Experimental determination of the isotopic ratio in the sample gave an atomic weight of 10.805 ± 0.004 which was used in calculating ΔH_r° . This value remains essentially unchanged in terms of the accepted atomic weight of 10.811 for natural boron.



Domalski and Armstrong (45) reported the combustion in fluorine of pelleted mixtures of boron and Teflon. The boron contributed roughly 35% of the energy. Corrections for impurities in the boron (0.12% metallic impurities and 0.20% C, O and N) amounted to about 0.24% of ΔE_c° (boron). Experimental determination of the isotopic ratio gave 10.812 ± 0.005 ; thus, the accepted atomic weight of 10.811 was used in calculating ΔH_r° . The authors' estimate of the overall experimental uncertainty is accepted instead of a value based only on random error (19).



Gunn (46) reported $\Delta\text{Hr}_{298}^\circ = -28.29 \pm 0.07 \text{ kcal/gfw}$ for the reaction $\text{BF}_3(\text{g}) + 15.67 \text{ HF}(3.747 \text{ H}_2\text{O}) \rightarrow [\text{solution}]$, while Good and Mansson (47) reported $\Delta\text{Hr}_{298}^\circ = -173.406 \pm 0.2 \text{ kcal/gfw}$ for $\text{B}(\text{c}, \beta) + 0.75 \text{ O}_2(\text{g}) + 18.57 \text{ HF}(3.065 \text{ H}_2\text{O}) \rightarrow [\text{solution}] + 1.5\text{H}_2\text{O}(\ell)$, where the resulting solutions have the same composition. A reduction to $\text{HF}(3.747 \text{ H}_2\text{O})$ of $+1.624 \text{ kcal/gfw}$ with an estimated uncertainty of 10 to 25%, or roughly 0.2 to 0.4 kcal/gfw, is applied to the latter reaction. The difference between the two reactions and a reduction to $\text{HF}(50 \text{ H}_2\text{O})$ of $+0.717 \pm 0.1 \text{ kcal/gfw}$ are used to obtain the result given above. The overall uncertainty is estimated as 0.3 to 0.5 kcal/gfw, depending on the choice of uncertainty for reduction to $\text{HF}(3.747 \text{ H}_2\text{O})$.

Input Data

The computer program (48) is a generalized version which allows $\Delta\text{Hf}_{298}^\circ$, $\Delta\text{Gf}_{298}^\circ$ and S_{298}° as variables; however, only $\Delta\text{Hf}_{298}^\circ$ is involved in this study. The program performs two functions: it edits the observations and then obtains the least squares adjustment. Editing consists of transforming the observations from the form given previously into the system of linear equations ready for solution.

The input to the program consists of (i) species with variables, (ii) species with fixed values, (iii) observations, and (iv) constraints, if any. There are seven variables in this study, namely, the values of $\Delta\text{Hf}_{298}^\circ$ for $\text{HF}(\text{g})$, $\text{HF}(50 \text{ H}_2\text{O})$, $\text{NaF}(\text{c})$, $\text{BF}_3(\text{g})$, $\text{NF}_3(\text{g})$, $\text{CF}_4(\text{g})$ and $\text{C}_2\text{F}_4(\text{polymer})$. Species with fixed values of $\Delta\text{Hf}_{298}^\circ$ are listed in Table I. These include nine elements or ions in their standard reference states and eleven compounds with enthalpies of formation which are assumed to be fixed. The twenty three observations, each consisting of the reaction,

enthalpy of reaction, and uncertainty, are summarized* in Table II. The last six columns in the table indicate variations in the observations which were used in six preliminary adjustments. No constraints are involved.

The edited observations, shown in Table III, summarize the relationships among the variables for the final adjustment (HF-7). All "fixed" species have been removed by substitution of their heats of formation and uncertainties. All uncertainties are assumed to be independent and are combined by use of Equation 17 of Rossini (19). The resulting values of $R_i \pm U_i$, involving only variables, provide the most direct comparison among the observations. Table III is also the most concise representation of the input data. It is the starting point for both sequential and simultaneous adjustments.

Results of the Simultaneous Adjustments

Results of the final adjustment (HF-7) and six preliminary adjustments (HF-1 through HF-6) are given in Table IV. Also shown is the least sum adjustment of HF-7. Below each least squares value of ΔH_f° is the corresponding standard error (54) based on the overall consistency rather than the internal consistency of each observation. This point will be emphasized in the discussion.

The preliminary adjustments represent various stages in the review of the input data as noted in Table II. All preliminary adjustments used our tentative estimate of 0.05 kcal/gfw for the uncertainty of R_3 rather than the proper value (23) of 0.10 kcal/gfw. The effect of this change is insignificant (cf. HF-7 and HF-6 in Table IV). Adjustments prior to HF-6 do not include R_7 ,

*Table II is an example of a catalog of observed thermochemical processes. Armstrong (12) has suggested the value of such catalogs. They summarize the input data used for adjustment, either sequential or simultaneous.

the heat of neutralization from Kolesov and Skuratov (28). Inclusion of this observation (cf. HF-7 and HF-4) changes the values of both HF(g) and NaF(c) by about +0.07 kcal/gfw and reduces the standard error of the latter from 0.11 to 0.07. Other changes are insignificant. The discussion of R12 indicates that the Teflon combustions of Wood et al. (34) and Armstrong (12,13) differ by 1 kcal/gfw or twice the sum of their uncertainties. When the value of Wood is substituted for that of Armstrong (cf. HF-5 and HF-4), C₂F₄(polymer) is changed by +0.7 kcal/gfw and CF₄(g) by +0.08 kcal/gfw. Adjustments prior to HF-4 use 0.3 rather than 0.5 kcal/gfw as the estimated uncertainty for R23. The only significant effect of this is to shift BF₃(g) from -271.42 to -271.29 kcal/gfw. Adjustments HF-3 and HF-2 indicate the effects of different combinations of R12, R12a and R12b. Omission of R6 and R19 has negligible effect (cf. HF-2 and HF-1), since these observations are relatively consistent but uncertain.

Not listed in Table IV are several other adjustments in which ϕ_L for HF(50 H₂O) was changed by ± 0.2 kcal/gfw and the uncertainty was reduced from 0.3 to 0.2 kcal/gfw. These results are not significantly different from those already tabulated.

Discussion

There is an excellent precedent for use of the simultaneous method in adjustments of overdetermined data. The fundamental constants of physics and chemistry, formerly treated via sequential adjustment by Birge (55), have been obtained for over two decades by simultaneous adjustment with the criterion of least squares (56,57,58). Experience derived from these studies of the physical constants will serve as the basis of the following discussion.

The species with fixed values in Table I correspond roughly to the "auxiliary constants" of physics (58). In this classification

are included standard reference states, which are zero by definition, and experimental values of relatively high accuracy. Since some of these experimental values have uncertainties comparable with the data to be analyzed, both the fixed values and their uncertainties are substituted into the observations.

Error assignments must be expressed on as comparable a basis as possible, since they are to be used in weighting the observations. Assignments for the HF system are based on the random uncertainty supplemented in some cases by estimates of the systematic uncertainty. Reliable estimates of the latter appear to be particularly important in the present system due to the common occurrence of side reactions. It must be emphasized that the observations are usually a combination of at least three measurements including an energy calibration, an energy determination, and an analysis of the amount of chemical reaction.

Cohen and DuMond (58) stressed the importance of overdetermination in testing the observations. They suggested that consistency of the data as a whole is the ultimate test, and that this test becomes more searching with each new path of measurement. It was this sort of testing which revealed the bias in early data for HF and prompted the new data analyzed herein. Overdetermination in this system remains extensive even after elimination of those experiments which are probably biased. The selected observations include only two variables which are involved in as few as three different experiments. The remainder are involved in from five to eight experiments.

Birge's ratio test may be used as a measure of the overall consistency of the data. Cohen and DuMond (58) noted that this ratio consists of the quotient of the external or a posteriori error with the internal or a priori error. The a priori error is derived from the uncertainties of the individual observations, while the a posteriori error is based on their deviations from

the adjustment. When the ratio is close to one, there is no strong evidence of the presence of systematic error. The ratio is evaluated from:

$$(\text{Birge's ratio})^2 = (\text{Chi})^2/(m-n) \quad (4)$$

$$\text{and} \quad (\text{Chi})^2 = \sum_{i=1}^m (E_i'/U_i)^2 \quad (5)$$

where E_i'/U_i is the weighted deviation or normalized residual.

Results of the ratio test are summarized in Table V. It may be concluded that there is no strong evidence of systematic error in HF-7, HF-6 and HF-4. Larger ratio values in the other adjustments suggest the possibility of systematic errors or underestimates of the a priori uncertainties. Sharp increases in the ratio occur with the inclusion of R12a and R12b due to their mutual inconsistency. In such cases, Cohen and DuMond (58) recommended the rejection of one or both observations upon location of a physical cause of unreliability in the experiment. Thus R12b is rejected on grounds suggested earlier and because our estimate of the uncertainty is based on inadequate information. Likewise, R12a is replaced with R12, which involves the later (and presumably more reliable) estimate of the uncertainty.

Individual deviations of the observations from the final adjustments by least squares and least sum are shown in the last four columns of Table III. Note that least sum assigns zero deviations to seven observations: R3, R7, R9, R12, R14, R18 and R20. These same observations in least squares have small but non-zero deviations, the largest magnitude being 0.18 kcal/gfw for R20.

The largest weighted deviations are -2.21 (R16), +2.04 (R1), +1.87 (R17) and +1.55 (R23). Most of the inconsistency is concentrated in these four observations. R1 is the direct measurement of HF(50 H₂O). R16, R17 and R23 are quite sensitive to

HF(50 H₂O) and they tend toward a more negative value than the direct measurement. The strain would be partially relieved by increasing the uncertainty of R1 to 0.09 kcal/gfw, which includes a reasonable estimate for systematic uncertainty (20). Lack of comparable estimates for R16, R17 and R23 makes this undesirable.

Sequential adjustments of the observations are not attempted in this paper. Interested readers may use Table III to make their own adjustments. It is likely that no two individuals will get the same answers, since the number of possible paths to each variable is quite large.

Cohen and DuMond (58) concluded that simultaneous adjustment by least squares is the logical approach in situations where there is considerable overdetermination. We agree concerning simultaneous adjustment, but also suggest that least squares is not the only logical criterion in a particular situation. Least sum considers all of the data, yet provides a logical means of selecting a preferred subset just sufficient to determine the constants. Cohen and DuMond (58) implied, to the contrary, that such a selection must ignore all of the other data. Least sum is also less sensitive to outlying observations than is least squares. It is true that a least sum adjustment is not necessarily unique. There may be multiple solutions in a particular case, but this has not appeared in our systems. It is not likely in cases with considerable overdetermination. We conclude that least sum is complementary with least squares and that the two should be used together whenever practical.

There is little reason to prefer one criterion over the other in the HF system. The only significant difference is that least sum agrees better with the direct determination (42) of BF₃(g). Preference for least sum could be based on the likelihood of outlying observations in this system. The difference is so small, however, that the least squares adjustment is preferred.

The selected values are summarized in Table VI, along with overall uncertainties estimated from twice the standard errors of the least squares adjustment. The user should be warned that the simple formula for propagation of errors (19) is only the first approximation when two or more of the selected values are combined in calculation of a third quantity. Correlation of errors (58) is likely among some of the selected values. This requires use of additional terms, which may be either positive or negative, in the general formula for propagation of errors (58,59). Interpretation of the derived uncertainties is further complicated, since the input data were weighted in some cases by inclusion of reasonable bounds for the systematic error.

Values of ΔH_{298}° for HF(*n* H₂O) should be obtained from that for HF(50 H₂O) using differences taken from the dilution curve of Parker (17). Additional error should be small, except for *n* > 1000. The values selected for HF(50 H₂O) and NaF(c) imply that Φ_L for HF(50 H₂O) is about 0.15 ± 0.2 kcal/gfw less positive than that tabulated by Parker (17). This difference arises partly from the heat of neutralization (28) and partly from other data.

The analysis reveals some paths which should receive further attention. Since NaF is so closely linked with HF(aq), it is most surprising that good, modern data are not available for the heat of neutralization of NaOH with HF or for the heat of dilution of NaF. Parker's estimate (17) for the latter is reasonable, but it should be verified by experimental data. New measurements of the heat of dilution of HF in dilute solutions would provide a sensitive means of testing the calculated Φ_L curve (cf. earlier discussion for R8). It has already been stressed that links such as R16 are very sensitive for testing the enthalpy of formation of HF(50 H₂O). Other links would add to the test. Finally, a thorough analysis of the data for HF(real gas) could remove the nonideality corrections as a source of uncertainty for HF(g).

Acknowledgment

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References

1. F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of Chemical Substances," Reinhold Publishing Corp., New York, 1936.
2. F. D. Rossini et al., "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1950.
3. D. D. Wagman et al., "Selected Values of Chemical Thermodynamic Properties," NBS Technical Note 270-1, 1965, and NBS Technical Note 270-3, 1968.
4. J. R. Rice, "The Approximation of Functions," Vol. I, Chapt. 1, Addison-Wesley Publishing Co., Reading, Mass., 1964.
5. A. Syverud and M. Klein, Progress Reports I, II, III, IV under National Bureau of Standards Contract CST-1165, The Dow Chemical Co., Midland, Mich., 1964-1965.
6. J. G. Hust and R. D. McCarty, *Cryog.*, 7, 200 (1967).
7. G. Forsythe and C. B. Moler, "Computer Solution of Linear Algebraic Systems," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1967.
8. A. Ralston and H. S. Wilf, "Mathematical Methods for Digital Computers," John Wiley & Sons, Inc., New York, 1964.
9. A. Ralston and H. S. Wilf, "Mathematical Methods for Digital Computers," Vol. II, John Wiley & Sons, Inc., New York, 1967.
10. Ref. (8), Chapter 25.
11. N. P. Loomba, "Linear Programming," McGraw-Hill Book Company, New York, 1964.
12. G. T. Armstrong, U. S. Nat. Bur. Stand., Report 9803, 1 (1968).
13. E. S. Domalski and G. T. Armstrong, J. Res. Nat. Bur. Stand., 71A, 105 (1967).
14. J. R. Lacher and H. A. Skinner, J. Chem. Soc., A1968, 1034.
15. E. Rudzitis, private communication, parts IV and V of "Thermodynamic Properties of Hydrogen Fluoride," Argonne National Laboratory, 1963 and 1965.

16. G. T. Armstrong and L. A. Krieger, U. S. Nat. Bur. Stand. Report 7192, 92 (1961).
17. V. B. Parker, "Thermal Properties of Aqueous Uni-Univalent Electrolytes," NSRDS-NBS 2, 1965.
18. JANAF Thermochemical Tables, The Dow Chemical Company, Midland, Mich., December 1968.
19. F. D. Rossini, Chapt. 14, "Experimental Thermochemistry," Interscience Publishers, Inc., New York, 1956.
20. R. C. King and G. T. Armstrong, J. Res. Nat. Bur. Stand., 72A, 113 (1968); NBS Report 9500, 140 (1967).
21. J. W. C. Johns and R. F. Barrow, Proc. Roy. Soc. (London), A251, 504 (1959).
22. W. W. Rodenburg and C. E. Vanderzee, paper presented at the 22nd Annual Calorimetry Conference, Thousand Oaks, Calif., June 1967.
23. C. E. Vanderzee, private communication, Univ. of Nebraska, Jan. 23, 1969.
24. L. G. Hepler, W. L. Jolly and W. M. Latimer, J. Amer. Chem. Soc., 75, 2809 (1953); W. M. Latimer and W. L. Jolly, *ibid.*, 1548 (1953); D. H. Davies and G. C. Benson, Can. J. Chem., 43, 3100 (1965).
25. J. P. Coughlin, J. Amer. Chem. Soc., 80, 1802 (1958); 79, 2397 (1957).
26. G. C. Hood and M. M. Woyski, J. Amer. Chem. Soc., 73, 2738 (1951).
27. H. von Wartenberg and O. Fitzner, Z. Anorg. Allgem. Chem., 151, 313 (1926).
28. V. P. Kolesov and S. M. Skuratov, Russ. J. Inorg. Chem. (Engl. Transl.), 6, 889 (1961).
29. J. D. Cox and D. Harrop, Trans. Faraday Soc., 61, 1328 (1965).
30. A. J. Ellis, J. Chem. Soc. 1963, 4300.
- 30a. T. Erdey-Gruz, L. Majthenye and E. Kugler, Acta Chim. Acad. Sci. Hung., 37, 393 (1963).

31. H. N. Farrer and F. J. C. Rossotti, J. Inorg. Nucl. Chem., 26, 1959 (1964).
32. E. Greenberg and W. N. Hubbard, J. Phys. Chem., 72, 222 (1968).
33. W. D. Good, D. W. Scott and G. Waddington, J. Phys. Chem., 60, 1080 (1956); J. Amer. Chem. Soc., 77, 245 (1955).
34. J. L. Wood, R. J. Lagow and J. L. Margrave, J. Chem. Eng. Data, 12, 255 (1967).
35. G. M. Martin and R. K. Eby, J. Res. Nat. Bur. Stand. 72A, 467 (1968).
36. J. D. Cox, H. A. Gundry and A. J. Head, Trans. Faraday Soc., 61, 1594 (1965).
37. L. C. Walker, paper presented at the 22nd Annual Calorimetry Conference, Thousand Oaks, Calif., June 1967.
38. G. C. Sinke, J. Chem. Eng. Data, 10, 295 (1965).
39. L. C. Walker, J. Phys. Chem., 71, 361 (1967).
40. G. C. Sinke, J. Phys. Chem., 71, 359 (1967).
41. J. R. Ludwig and W. J. Cooper, J. Chem. Eng. Data, 8, 76 (1963).
42. G. K. Johnson, H. M. Feder and W. N. Hubbard, J. Phys. Chem., 70, 1 (1966).
43. S. S. Wise, J. L. Margrave, H. M. Feder and W. N. Hubbard, J. Phys. Chem., 65, 2157 (1961).
44. P. Gross, C. Hayman and M. C. Stuart, Proc. Brit. Ceram. Soc. 1967, 39.
45. E. S. Domalski and G. T. Armstrong, J. Res. Nat. Bur. Stand., 71A, 195 (1967).
46. S. R. Gunn, J. Phys. Chem., 69, 1010 (1965).
47. W. D. Good and M. Mansson, J. Phys. Chem., 70, 97 (1966).
48. A. N. Syverud, "Simultaneous Adjustment of ΔH_f° , ΔG_f° and S° by Least Squares," The Dow Chemical Company, Midland, Mich., Oct. 29, 1969.
49. Value assigned in this study.

50. S. R. Gunn and L. G. Green, J. Chem. Eng. Data, 8, 180 (1963); S. R. Gunn, UCRL-7992, Livermore, Calif., July 29, 1964.
51. C. E. Vanderzee and J. D. Nutter, J. Phys. Chem., 67, 2521 (1963).
52. S. R. Gunn, J. Phys. Chem., 71, 1386 (1967).
53. P. A. G. O'Hare, J. L. Settle and W. N. Hubbard, Trans. Faraday Soc., 62, 558 (1966).
54. Ref. 8, Chapter 17.
55. R. T. Birge, Rev. Mod. Phys., 1, 1 (1929).
56. F. G. Dunnington, Rev. Mod. Phys., 11, 68 (1939).
57. E. R. Cohen, K. M. Crowe and J. W. M. DuMond, "The Fundamental Constants of Physics," Interscience Publishers, Inc., New York, 1957.
58. E. R. Cohen and J. W. M. DuMond, Rev. Mod. Phys., 37, 537 (1965).
59. Ref. 57, Chapter 7.
60. M. F. Guest, J. B. Pedley and M. Horn, J. Chem. Thermodyn. 1, 345 (1969).
61. A. N. Syverud, The Dow Chemical Co., Midland, Mich., Quarterly Technical Report AFRPL-TR-69-70, Jan. 1969, Contract FO4611-67-C-0009.
62. E. Constantinides, "The Thermochemistry of Hydrofluoric Acid," published by the author, London, 1969.

Table I
Species with Fixed Values of $\Delta H_f^\circ_{298}$

<u>Species</u>	<u>$\Delta H_f^\circ_{298}$, kcal/gfw</u>	<u>Reference</u>
B(c, β)	0.0 \pm 0.0	Defined
C(graphite)	0.0 \pm 0.0	Defined
Cl ₂ (g)	0.0 \pm 0.0	Defined
CO ₂ (g)	-94.051 \pm 0.030	(3)
C ₂ N ₂ (g)	73.84 \pm 0.43	(3)
F(g)	18.86 \pm 0.3	(18, 49)
F ₂ (g)	0.0 \pm 0.0	Defined
H(g)	52.095 \pm 0.002	(3)
HCl(g)	-22.062 \pm 0.02	(3)
HCl(aq)	-39.932 \pm 0.02	(49, 50, 51)
H ⁺ (aq)	0.0 \pm 0.0	Defined
H ₂ (g)	0.0 \pm 0.0	Defined
H ₂ O(l)	-68.315 \pm 0.01	(3)
N ₂ (g)	0.0 \pm 0.0	Defined
NaCl(c)	-98.32 \pm 0.06	(49, 52)
NaOH(aq)	-112.44 \pm 0.04	(49, 52)
Na ⁺ (aq)	-57.47 \pm 0.04	(49, 52)
O ₂ (g)	0.0 \pm 0.0	Defined
S(c, rh)	0.0 \pm 0.0	Defined
SF ₆ (g)	-291.77 \pm 0.24	(53)

Table II
Observations Used for Simultaneous Adjustments

No.	Reaction	Adjustment No. →	ΔH_{298}° kcal/gfw HF-7	HF-6	HF-5	HF-4	HF-3	HF-2	HF-1
1	$0.5 \text{ H}_2(\text{g}) + 0.5 \text{ F}_2(\text{g}) \rightarrow \text{HF}(50 \text{ H}_2\text{O})$		-76.68±0.05						
2	$\text{HF}(\text{g}) \rightarrow \text{H}(\text{g}) + \text{F}(\text{g})$		136.051±0.3						
3	$\text{HF}(\text{g}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaF}(\text{c}) + \text{H}_2\text{O}(\ell)$		-28.24±0.10	±0.05	±0.05	±0.05	±0.05	±0.05	±0.05
4	$\text{HF}(50 \text{ H}_2\text{O}) + \text{NaCl}(\text{c}) \rightarrow \text{NaF}(\text{c}) + \text{HCl}(\text{aq})$		-2.41±0.07						
5	$\text{HF}(\text{g}) + \text{NaCl}(\text{c}) \rightarrow \text{NaF}(\text{c}) + \text{HCl}(\text{g})$		3.81±0.25						omit
6	$0.5 \text{ F}_2(\text{g}) + \text{NaCl}(\text{c}) \rightarrow \text{NaF}(\text{c}) + 0.5 \text{ Cl}_2(\text{g})$		-39.30±0.4						omit
7	$\text{HF}(50 \text{ H}_2\text{O}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaF}(\text{c}) + \text{H}_2\text{O}(\ell)$		-16.57±0.05		omit	omit	omit	omit	omit
8	$\text{H}^+(\text{aq}) + \text{NaF}(\text{c}) \rightarrow \text{HF}(50 \text{ H}_2\text{O}) + \text{Na}^+(\text{aq})$		3.41'±0.3						
9	$\text{C}(\text{graph}) + 2\text{F}_2(\text{g}) \rightarrow \text{CF}_4(\text{g})$		-223.05±0.18						
10	$\text{C}_2\text{F}_4(\text{polymer}) + \text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\ell) \rightarrow 4\text{HF}(50 \text{ H}_2\text{O}) + 2\text{CO}_2(\text{g})$		-160.62±0.9						
11	$\text{C}_2\text{F}_4(\text{polymer}) + \text{O}_2(\text{g}) \rightarrow \text{CF}_4(\text{g}) + \text{CO}_2(\text{g})$		-118.8±0.5						
12	$\text{C}_2\text{F}_4(\text{polymer}) + 2\text{F}_2(\text{g}) \rightarrow 2\text{CF}_4(\text{g})$		-247.85±0.3						
13	$\text{C}(\text{graph}) + 2\text{F}_2(\text{g}) \rightarrow \text{CF}_4(\text{g})$		-222.87±0.38						
14	$\text{CF}_4(\text{g}) + 2\text{H}_2\text{O}(\ell) \rightarrow 4\text{HF}(50 \text{ H}_2\text{O}) + \text{CO}_2(\text{g})$		-41.506±0.3						
15	$8\text{NF}_3(\text{g}) + 3\text{C}_2\text{N}_2(\text{g}) \rightarrow 6\text{CF}_4(\text{g}) + 7\text{N}_2(\text{g})$		-1308.8±1.3						
16	$\text{NF}_3(\text{g}) + 1.5\text{H}_2(\text{g}) \rightarrow 2\text{HF}(50 \text{ H}_2\text{O}) + 0.5\text{N}_2(\text{g})$		-199.4±0.22						
17	$2\text{NF}_3(\text{g}) + \text{S}(\text{c, rh}) \rightarrow \text{SF}_6(\text{g}) + \text{N}_2(\text{g})$		-228.26±0.25						
18	$\text{NF}_3(\text{g}) \rightarrow 0.5\text{N}_2(\text{g}) + 1.5\text{F}_2(\text{g})$		31.44±0.3						
19	$\text{NF}_3(\text{g}) + \text{B}(\text{c, } \beta) \rightarrow \text{BF}_3(\text{g}) + 0.5\text{N}_2(\text{g})$		-239.46±1.2						omit
20	$1.5 \text{ F}_2(\text{g}) + \text{B}(\text{c, } \beta) \rightarrow \text{BF}_3(\text{g})$		-271.6±0.9						
21	$1.5 \text{ F}_2(\text{g}) + \text{B}(\text{c, } \beta) \rightarrow \text{BF}_3(\text{g})$		-271.65±0.22						
22	$1.5 \text{ F}_2(\text{g}) + \text{B}(\text{c, } \beta) \rightarrow \text{BF}_3(\text{g})$		-271.03±0.51						
23	$3\text{HF}(50 \text{ H}_2\text{O}) + \text{B}(\text{c, } \beta) + 0.75 \text{ O}_2(\text{g}) \rightarrow \text{BF}_3(\text{g}) + 1.5\text{H}_2\text{O}(\ell)$		-142.77±0.5				±0.3	±0.3	±0.3

*Uncertainty for Reaction 12b in HF-3 is assigned as 0.4 rather than 0.2 kcal/gfw.

Table III. Relationships among the Variables as Obtained from the Input for Final Adjustment (HF-7)

\underline{i}	Relationships among ΔH_{298}^0 Variables	$R_1 + U_1$, kcal/gfw	Least Squares		Least Sum	
			Dev.*	Dev./ U_1	Dev.*	Dev./ U_1
1	HF(50 H ₂ O)	-76.680±0.050	0.102	2.035	0.104	2.075
2	-HF(g)	65.096±0.424	-0.040	-0.094	-0.018	-0.042
3	NaF(c) - HF(g)	-72.365±0.108	0.015	0.135	0.0	0.0
4	NaF(c) - HF(50 H ₂ O)	-60.798±0.094	-0.064	-0.680	-0.103	-1.096
5	NaF(c) - HF(g)	-72.448±0.258	-0.068	-0.265	-0.083	-0.322
6	NaF(c)	-137.620±0.404	-0.104	-0.258	-0.141	-0.350
7	NaF(c) - HF(50 H ₂ O)	-60.695±0.065	0.039	0.600	0.0	0.0
8	-[NaF(c) - HF(50 H ₂ O)]	60.884±0.303	0.150	0.496	0.189	0.624
9	CF ₄ (g)	-223.050±0.180	-0.015	-0.083	0.0	0.0
10	4 x HF(50 H ₂ O) - C ₂ F ₄ (polymer)	-109.148±0.902	-0.239	-0.265	-0.263	-0.292
11	CF ₄ (g) - C ₂ F ₄ (polymer)	-24.749±0.501	0.068	0.136	0.051	0.102
12	2 x CF ₄ (g) - C ₂ F ₄ (polymer)	-247.850±0.300	0.002	0.007	0.0	0.0
13	CF ₄ (g)	-222.870±0.380	0.165	0.434	0.180	0.474
14	4 x HF(50 H ₂ O) - CF ₄ (g)	-84.685±0.302	0.007	0.023	0.0	0.0
15	6 x CF ₄ (g) - 8 x NF ₃ (g)	-1087.280±1.831	-0.116	-0.282	-0.500	-0.273
16	3 x HF(50 H ₂ O) - NF ₃ (g)	-199.400±0.220	-0.436	-2.207	-0.489	-2.222
17	-2 x NF ₃ (g)	63.510±0.347	0.648	1.871	0.630	1.816
18	-NF ₃ (g)	31.440±0.300	0.009	0.030	0.0	0.0
19	BF ₃ (g) - NF ₃ (g)	-239.460±1.200	0.529	0.441	0.700	0.583
20	BF ₃ (g)	-271.600±0.900	-0.180	-0.200	0.0	0.0
21	BF ₃ (g)	-271.650±0.220	-0.230	-1.045	-0.050	-0.227
22	BF ₃ (g)	-271.030±0.510	0.390	0.765	0.570	1.118
23	BF ₃ (g) - 3 x HF(50 H ₂ O)	-40.297±0.500	0.777	1.554	0.952	1.904
		Sum of Absolute values =	13.906		13.517	
		Sum of squares =	18.436		20.013	

*Dev. = E_1' = Observed value minus calculated value in kcal/gfw.

Table IV
Values of ΔH_f° from the Simultaneous Adjustments

Species	Least Sum kcal/gfw HF-7	Least Squares*							
		HF-7	HF-6	HF-5	HF-4	HF-3	HF-2	HF-1	
HF(g)	-65.114	-65.136	-65.144	-65.209	-65.210	-65.224	-65.224	-65.223	
		0.122	0.094	0.132	0.119	0.138	0.188	0.204	
H ₂ O	-76.784	-76.782	-76.782	-76.779	-76.781	-76.795	-76.796	-76.796	
		0.040	0.040	0.045	0.040	0.046	0.062	0.067	
NaF(c)	-137.479	-137.516	-137.515	-137.581	-137.583	-137.596	-137.597	-137.596	
		0.068	0.068	0.111	0.100	0.116	0.158	0.173	
BF ₃ (g)	-271.600	-271.420	-271.420	-271.419	-271.420	-271.285	-271.286	-271.293	
		0.195	0.195	0.218	0.196	0.210	0.285	0.307	
NF ₃ (g)	-31.440	-31.431	-31.431	-31.414	-31.430	-31.437	-31.442	-31.438	
		0.124	0.124	0.138	0.125	0.145	0.197	0.211	
CF ₄ (g)	-223.050	-223.035	-223.035	-222.949	-223.034	-223.020	-223.044	-223.043	
		0.140	0.140	0.155	0.141	0.164	0.219	0.234	
C ₂ F ₄ (polymer)	-198.250	-198.218	-198.218	-198.900	-198.216	-198.476	-198.284	-198.283	
		0.351	0.351	0.354	0.353	0.388	0.447	0.478	

*The number immediately below ΔH_f° is the standard error (54) based on the overall consistency of the least squares adjustment.

Table V

Statistical Summary of the Simultaneous Adjustments

Adjustment No.	Unknowns n	Observa- tions*,m	Degrees of Freedom,(m-n)	(Chi) ²	Birge's Ratio**
HF-7	7	23	16	18.44	1.073
(Least Sum)	7	23	16	(20.01)	(1.118)
HF-6	7	23	16	18.45	1.074
HF-5	7	22	15	21.46	1.196
HF-4	7	22	15	17.46	1.079
HF-3	7	23	16	25.37	1.259
HF-2	7	23	16	46.77	1.710
HF-1	7	21	14	46.66	1.826

*Changes in the observations are shown in Table II.

**See Equations 4 and 5.

Table VI

Selected Values of $\Delta H_f^{\circ}_{298}$

Species	$\Delta H_f^{\circ}_{298}$, kcal/gfw
HF(g)	-65.14 \pm 0.2
HF(50 H ₂ O)	-76.78 \pm 0.1
HF(∞ H ₂ O)	-79.82 \pm 0.2
NaF(c)	-137.52 \pm 0.15
BF ₃ (g)	-271.42 \pm 0.4
NF ₃ (g)	-31.43 \pm 0.3
CF ₄ (g)	-223.04 \pm 0.3
C ₂ F ₄ (polymer)	-198.2 \pm 0.7

APPENDIX B

Simultaneous Adjustment of Thermochemical Data
Enthalpies of Formation of C₂F₄, CF₃ and Six CF₃X Molecules
 by

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INTRODUCTION

Until very recently important uncertainties existed in the enthalpies of formation of gaseous C₂F₄, CF₃, and CF₃X (X = H, Cl, Br, I, CN, and CF₃). Values of $\Delta H_f^{\circ}_{298}$ selected (38) from the data available from about 1964 to 1966 were either incomplete or involved errors ranging from 1 to 11 kcal/gfw. Much of the error was due to inadequate characterization of the experiments and to biased auxiliary values, e.g. ΔH_f° for HF and CF₄. Errors in these auxiliary values have now been minimized by recent data (35).

Recent studies also provide an overdetermined set of consistent interrelations among the enthalpies of formation of CF₃ and CF₃X (X = H, Cl, Br, I, CN, and CF₃). Calorimetric and equilibrium data provide several paths for obtaining ΔH_f° of the CF₃X molecules, and kinetic data provide numerous links to the CF₃ radical. When such overdetermination exists, simultaneous adjustment is the most efficient way to select enthalpies of formation (35). This paper presents the simultaneous adjustment carried out during preparation of new JANAF Thermochemical Tables (18) for C₂F₄, CF₃ and CF₃X.

Methods of Reduction and Adjustment

Simultaneous adjustment (35) presumes that the data for each reaction may be reduced to values of $\Delta H_r^{\circ}_{298.15}$. Substitution of any known enthalpies of formation yields $R_i \pm U_i$, the observed value of some linear combination of the unknowns. "Best" approximations for the unknowns, $\Delta H_f^{\circ}_{298.15} = F_j'$, are then obtained by

minimizing a suitable function of the normalized residual (6), E_1'/U_1 , or weighted deviation. E_1' is the deviation between the observation and the adjustment:

$$E_1' = R_1 - \sum_j v_{1j} F_j'$$

where v_{1j} is the stoichiometric coefficient for species j in reaction i . The criterion of least squares is used in this paper. Lack of time precluded the use of the alternative criterion of least (absolute) sum (35).

Methods of reduction of the data are the same as those used previously (35). Auxiliary data for aqueous species are from Parker (27). Other thermodynamic functions are from the JANAF Thermochemical Tables (18). Overall uncertainty intervals are assigned and combined as recommended by Rossini (30). When values are derived from equilibrium or kinetic data, the reduction is less straightforward and is described below.

Equilibrium data have been reduced by second- and third-law analysis (29,33). ΔH_{298}° is taken as the mean of the third-law values derived from the individual equilibrium constants. Adoption of the mean is justified by the smallness of the inconsistencies within and among the sets of data.

The uncertainty in ΔH_{298}° is estimated as the larger of two terms, either the precision index of the individual third-law values or the estimated uncertainty in the product $T\Delta S_T^\circ$. The index of precision is taken as twice the standard deviation of single observations (30); this value usually exceeds the range of the individual third-law values. Uncertainty in the entropy arises mainly from neglect of anharmonic and rotational-distortion corrections in the calculation of the entropies of the CF_3X molecules (18). The equilibrium reactions involve two such molecules, one as a reactant and one as a product. There should be partial cancellation of the two uncertainties in terms of ΔS° ; thus,

the two are not combined. Instead, the uncertainty in ΔS_r° is assumed to be equal to the larger of the two values.

Thermodynamic functions for CF_3CN (g), not yet available in the JANAF Thermochemical Tables (18), have been taken from rigid-rotator-harmonic-oscillator calculations. These use a ground state quantum weight of 1, a symmetry number of 3, wave numbers (12) and degeneracies of 2271(1), 1228(1), 801(1), 521(1), 1215(2), 625(2), 464(2), 192(2), and product of the moments of inertia (36) of $1.1865 \times 10^{-113} \text{ g}^3 \text{ cm}^6$.

Kinetic data yield activation energies for the forward and reverse reactions. These have been combined at the temperature of the forward reaction and then reduced to 298.15°K using the appropriate enthalpies (18). In some cases it was necessary to assume that the reverse activation energy is independent of temperature. Such assumptions are reflected in the assigned uncertainties.

The final reduction for each reaction consists of removal of all species for which ΔH_f° is presumed to be known. Substitution for these species is done by computer (35) using the "fixed" values and uncertainties given in Table I.

Review of Data

Calorimetric data used in the adjustment are given in Table II. The JANAF Thermochemical Tables (18) for C_2F_4 , C_2F_6 , and CClF_3 discuss other data omitted due to large uncertainties.

The combustion of CHF_3 in oxygen ($i = 5$) involved formation of CF_4 in a competing reaction (25). Correction of each combustion using current data for CF_4 (see Table I) yields the mean value of $\Delta H_r^\circ = -90.35 \pm 0.7 \text{ kcal/gfw}$ for the final state of $\text{HF}(21.5 \text{ H}_2\text{O})$. The individual values show a serious trend with

the amount of competing reaction; extrapolation to zero competing reaction would make ΔH_r° more negative by about 1.6 kcal/gfw. Possible causes for this trend include corrosion and error in the analyses for CO_2 and HF. The authors tried to minimize the effect of corrosion by running the calibrations with HF present. We select the mean value of ΔH_r° , since it is more consistent with other data, and we increase the uncertainty to 1.0 kcal/gfw because the situation is ambiguous.

Equilibrium data used in the adjustment are given in Table III. Four of the reactions ($i = 6, 7, 9, 10$) yield entropy differences which are greater than the combined errors in the second-law and statistical values of $\Delta S_{r,T}^\circ$. The discrepancies are relatively small and cannot be traced to a single species. For example, CF_3Br occurs in five reactions, but only three have discrepancies. In both cases the signs of the discrepancies include both plus and minus. The logical conclusion is that the equilibrium data yield no systematic evidence of bias in the statistical entropies (18).

The mass-spectrometric study (13) of $2\text{C}(\text{graphite}) + 4\text{CF}_3(\text{g}) \rightarrow 3\text{C}_2\text{F}_4(\text{g})$ is grossly discrepant and has been omitted from the adjustment. Equilibrium is not attained between the gases and the effusion cell made of graphite. Reaction of CF_3 with graphite apparently yields a steady-state concentration of C_2F_4 which is much greater than the equilibrium value. Analogous behavior has been observed in the C-H system (22,32).

Values derived from kinetic data are given in Table IV. Data for CF_3 based on the many studies by electron impact and photoionization have been omitted due to uncertainty in the excess energies of the ions. The thorough discussion of photoionization data by Noutary (26) emphasized that CF_3^+ is formed with large amounts of excess energy both during ionization of CF_3 and during fragmentation of fluorides. The amount of excess energy varies with the

parent molecule. This difficulty may also affect the electron impact studies and could account for some of the discrepancies in bond dissociation energies derived from appearance potentials and ionization potentials. Electron impact data have been summarized by Coomber (10).

Results of the Adjustment

Table V summarizes the twenty observations after final reduction. Deviations from the least-squares adjustment are given in the last two columns. The weighted deviations, all of them less than 1.0, yield the very small Birge's ratio (35, 6) of 0.69. This indicates a high degree of consistency among the observed values and their assigned uncertainties.

Enthalpies of formation obtained by the adjustment are given in the second column of Table VI. Uncertainties are assigned as twice the standard error (35) derived from the adjustment. These uncertainties indicate the magnitudes of the probable errors in the enthalpies of formation; however, they are only first approximations (6, 35) when used in the simple formula for propagation of errors (30).

The uncertainty for any species depends, in general, on the other species being combined with it. For example, consider the uncertainty in ΔH_r° for the bromination of CF_3H ($i = 7$ in Table III). The simple propagation formula predicts an uncertainty of 1.07 kcal/gfw, but the experimental uncertainty of 0.3 kcal/gfw is more nearly correct. The uncertainties of CF_3H and CF_3Br are said to be correlated in the statistical sense (6), and assignment of the proper error in ΔH_r° requires use of the correlation coefficients. These are not printed out by the present computer program. Note that each of the observations used in the adjustment is a possible case of correlation of errors. Observation $i = 7$ is the extreme case; similar, but less serious, error correlations probably exist for $i = 6, 9, 10$, and 19.

Table VI also compares the adjusted values with previous selections. There is excellent agreement with the values of Lacher and Skinner (20). These were obtained by applying the long-established method of sequential adjustment to a subset of the observations considered in this paper. The earlier selections of the National Bureau of Standards (38) reflect the less reliable data available about 1964.

Values of $DH^\circ (F_3C-X)$ may be calculated from the results of Table VI using enthalpies of formation for the X radicals. Taking the latter from Table I and (18), we obtain the standard bond dissociation energies (4) given in Table VII. These may be compared with the analogous values of $DH^\circ (H_3C-X)$ based on enthalpies of formation from recent reviews (20,34). A discussion of the bond dissociation energies will be given separately (28).

Conclusions

Simultaneous adjustment of recent data leads to consistent enthalpies of formation for C_2F_4 , CF_3 , and CF_3X ($X = H, Cl, Br, I, CN$, and CF_3) in the ideal-gas states. The considerable overdetermination in the data lends credence to the reliability of the results. Derived dissociation energies for the C-X bond in CF_3X should also be reliable.

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NOMENCLATURE

DH° = standard bond dissociation energy
 E' = deviation of observed R from adjusted value
 F' = adjusted value of ΔH_f°
 ΔH_f° = standard enthalpy of formation
 ΔH_r° = standard enthalpy of reaction
 R = observed ΔH_r° after substitution for "fixed" ΔH_f°
 ΔS_r° = standard entropy of reaction
 T = temperature, $^\circ K$
 U = uncertainty in R
 δ = difference between second-law and statistical values of ΔS_r°
 e = estimated uncertainty in statistical value of ΔS_r°
 v = stoichiometric coefficient

Subscripts:

i = reaction index
 j = chemical species index

References

1. Amphlett, J. C., Whittle, E., Trans. Faraday Soc., 62, 1662 (1966).
2. Ibid., 64, 2130 (1968).
3. Arthur, N. L., Gray, P., Ibid., 65, 434 (1969).
4. Benson, S. W., J. Chem. Educ., 42, 502 (1965).
5. Boyd, R. K., Downs, G. W., Gow, J. S., Horrex, C., J. Phys. Chem., 67, 719 (1963).
6. Cohen, E. R., DuMond, J. W. M., Rev. Mod. Phys. 37, 537 (1965).
7. Coomber, J. W., Whittle, E., Trans. Faraday Soc., 62, 2183 (1966).
8. Ibid., 63, 608 (1967).
9. Ibid., p. 1394.
10. Ibid., p. 2656.
11. Douglas, A. E., Moller, C. K., Stoicheff, B. P., Can. J. Phys., 41, 1174 (1963).
12. Edgell, W. F., Potter, R. M., J. Chem. Phys., 24, 80 (1956).
13. Ehlert, T. C., J. Phys. Chem., 73, 949 (1969).
14. Giles, R. D., Whittle, E., Trans. Faraday Soc., 61, 1425 (1965).
15. Goy, C. A., Lord, A., Pritchard, H. O., J. Phys. Chem., 71, 1086 (1967).
16. Horsley, J. A., Barrow, R. F., Trans. Faraday Soc., 63, 32 (1967).
17. Howard, P. B., Skinner, H. A., J. Chem. Soc., A1966, 1536.
18. JANAF Thermochemical Tables, The Dow Chemical Company, Midland, Michigan, July 1969.
19. Kolesov, V. P., Zenkov, I. D., Skuratov, S. M., Zh. Fiz. Khim., 36, 89 (1962); J. Phys. Chem. USSR, 36, 45 (1962).
20. Lacher, J. R., Skinner, H. A., J. Chem. Soc., A1968, 1034.
21. Laurence, G. S., Trans. Faraday Soc., 63, 1155 (1967).
22. Lifshitz, C., Chupka, W. A., J. Chem. Phys., 48, 1109 (1968).

23. Lord, A., Goy, C. A., Pritchard, H. O., J. Phys. Chem., 71, 2705 (1967).
24. Neugebauer, C. A., Margrave, J. L., Ibid., 60, 1318 (1956).
25. Ibid., 62, 1043 (1958).
26. Noutary, C. J., J. Res. Nat. Bur. Stand., 72A, 479 (1968).
27. Parker, V. B., "Thermal Properties of Aqueous Uni-univalent Electrolytes," NSRDS-NBS-2, 1965.
28. Perettie, D. J., Walker, L. C., Sinke, G. C., Janz, G. J., submitted for publication in J. Amer. Chem. Soc.
29. Prophet, H., Syverud, A. N., Justice, B. H., presented at the 23rd Annual Calorimetry Conference, Midland, Mich., August 1968.
30. Rossini, F. D., "Experimental Thermochemistry," Interscience Publishers, Inc., New York, 1956, Chapter 14.
31. Sinke, G. C., J. Phys. Chem., 70, 1326 (1966).
32. Steck, S. J., Pressley, G. A., Lin, S., Stafford, F. E., J. Chem. Phys., 50, 3196 (1969).
33. Stull, D. R., Prophet, H., in "The Characterization of High-Temperature Vapors," J. L. Margrave, Ed., John Wiley & Sons, Inc., New York, 1967, Chapter 13.
34. Stull, D. R., Westrum, E. F., Sinke, G. C., "The Chemical Thermodynamics of Organic Compounds," John Wiley & Sons, Inc., New York, 1969.
35. The Dow Chemical Co., Midland, Mich., Quarterly Technical Report AFRPL-TR-69-70, Jan. 1969, Contract F04611-67-C-0009.
36. Thomas, L. F., Heeks, J. S., Sheridan, J., Z. Elektrochem., 61, 935 (1957).
37. Tschuikow-Roux, E., J. Chem. Phys., 43, 2251 (1965).
38. Wagman, D. D., Evans, W. H., Parker, V. B., Halow, I., Bailey, S. M., Schumm, R. H., "Selected Values of Chemical Thermodynamic Properties," Nat. Bur. Stand. Tech. Note 270-1, 1965, and 270-3, 1968.

Table I
Species with Fixed Enthalpies of Formation^a

<u>Species</u>	<u>$\Delta H_f^\circ_{298}$, kcal/gfw</u>	<u>Reference</u>
Br(g)	26.73 \pm 0.03	(16,38,18) ^b
Br ₂ (g)	7.387 \pm 0.03	(38,18)
CF ₄ (g)	-223.04 \pm 0.3	(35,18)
CH ₃ (g)	34.82 \pm 0.2	(18)
CH ₄ (g)	-17.88 \pm 0.08	(38,18)
CO ₂ (g)	-94.051 \pm 0.03	(38,18)
C ₂ N ₂ (g)	73.84 \pm 0.43	(38)
Cl(g)	28.99 \pm 0.1	(11,18) ^b
ClBr(g)	3.50 \pm 0.3	(38,18)
HBr(g)	-8.70 \pm 0.1	(38,18)
HCl(g)	-22.062 \pm 0.02	(38,18)
HF(g)	-65.14 \pm 0.2	(35,18)
HF(50 H ₂ O)	-76.78 \pm 0.1	(35,18)
HI(g)	6.33 \pm 0.6	(38) ^{b,c}
H ₂ O(l)	-68.315 \pm 0.01	(38)
I(g)	25.535 \pm 0.02	(38,18)
IBr(g)	9.77 \pm 0.04	(38)
ICl(g)	4.18 \pm 0.05	(18)
I ₂ (g)	14.923 \pm 0.02	(38,18)
NF ₃ (g)	-31.43 \pm 0.3	(35,18)
NaF(c)	-137.52 \pm 0.15	(35,18)

^aOther species with fixed values are the chemical elements in their standard reference states; these are zero by definition.

^bValues assigned in this study.

^cUncertainty increased to overlap the calorimetric result of (17).

Table II
Calorimetric Data

Ref.	Reaction	ΔH_{298}° kcal/gfw	1
(24)	$C_2F_4(g) \rightarrow CF_4(g) + C(\text{graphite})$	-65.4 \pm 0.5	1
(24)	$C_2F_4(g) + 2H_2(g) \rightarrow 2C(\text{graphite}) + 4HF(50\ H_2O)$	-150.9 \pm 1.2	2
(19)	$C_2F_4(g) + 4Na(c) \rightarrow 2C(\text{graphite}) + 4NaF(c)$	-392.9 \pm 1.3	3
(31)	$1.5C_2F_6(c) + NF_3(g) \rightarrow 3CF_4(g) + 0.5N_2(g)$	-155.8 \pm 1.5	4
(25)	$CHF_3(g) + 0.5O_2(g) + H_2O(l) \rightarrow CO_2(g) + 3HF(50\ H_2O)$	-90.43 \pm 1.0 ^a	5
(28)	$3CF_3CN(g) + 5NF_3(g) \rightarrow 6CF_4(g) + 4N_2(g)$	-824.4 \pm 0.6	20

^aData recalculated as discussed in the text.

Table III
Reduction of Equilibrium Data by Second- and Third-Law Analysis

Ref.	Reaction	Range T°K	Entropy Tests gibbs/gfw			ΔH_{298}° , kcal/gfw			1
			δ^a	b^b	c	2nd Law	3rd Law	Adopted	
(9)	$C_2F_6(g)+Br_2(g) \rightarrow 2CF_3Br(g)$	894- 995	2.5 ± 1.0	0.7		5.68 ± 0.99	3.30 ± 0.32	3.30 ± 0.7	6
(8)	$CF_3H(g)+Br_2(g) \rightarrow CF_3Br(g)+HBr(g)$	684- 881	-1.8 ± 0.3	0.4		-5.94 ± 0.23	-4.55 ± 0.27	-4.55 ± 0.3	7
(15)	$CF_3H(g)+I_2(g) \rightarrow CF_3I(g)+HI(g)$	653- 802	-0.4 ± 1.5	0.5		16.82 ± 1.10	17.11 ± 0.55	17.11 ± 0.55	8
(23)	$CF_3Br(g)+I_2(g) \rightarrow CF_3I(g)+IBr(g)$	637- 739	1.1 ± 0.2	0.5		10.39 ± 0.14	9.60 ± 0.09	9.60 ± 0.4	9
(23)	$CF_3Cl(g)+I_2(g) \rightarrow CF_3I(g)+ICl(g)$	620- 732	-3.5 ± 1.4	0.5		14.92 ± 0.96	17.28 ± 0.39	17.28 ± 0.4	10
(10)	$CF_3Br(g)+Cl_2(g) \rightarrow CF_3Cl(g)+BrCl(g)$	832-1019	-0.4 ± 0.7	0.4		-11.14 ± 0.63	-10.77 ± 0.32	-10.77 ± 0.4	11
(10)	$CF_3Cl(g)+Br_2(g) \rightarrow CF_3Br(g)+BrCl(g)$	829- 934	0.2 ± 1.5	0.4		10.80 ± 1.32	10.58 ± 0.42	10.58 ± 0.4	12
$\frac{1}{2}(28)$	$C_2F_6(g)+C_2N_2(g) \rightarrow 2CF_3CN(g)$	865- 925	0.0 ± 1.5	0.6		10.62 ± 1.33	$10.59 \pm .20$	10.59 ± 0.5	19

$a_\delta = [\Delta S_r^\circ(2nd\ law) - \Delta S_r^\circ(statistical)] \pm [\text{uncertainty in } \Delta S_r^\circ(2nd\ law) \text{ from least squares fit}]$

$b_e = \text{Estimated uncertainty in } \Delta S_r^\circ(statistical); \text{ see text.}$

Table IV
Values Derived from Kinetic Data

<u>Ref.</u>	<u>Reaction</u>	<u>$\Delta H_{298.15}^{\circ}$ kcal/gfw</u>	<u>i</u>
(7,3,1)	$\text{CF}_3\text{H}(\text{g}) + \text{Cl}(\text{g}) \rightarrow \text{CF}_3(\text{g}) + \text{HCl}(\text{g})$	2.93 ± 0.7	13
(2,3)	$\text{CF}_3\text{H}(\text{g}) + \text{Br}(\text{g}) \rightarrow \text{CF}_3(\text{g}) + \text{HBr}(\text{g})$	18.89 ± 0.5	14
(15)	$\text{CF}_3\text{H}(\text{g}) + \text{I}(\text{g}) \rightarrow \text{CF}_3(\text{g}) + \text{HI}(\text{g})$	35.5 ± 3	15
(15,21,5)	$\text{CF}_3\text{I}(\text{g}) + \text{I}(\text{g}) \rightarrow \text{CF}_3(\text{g}) + \text{I}_2(\text{g})$	17.1 ± 2	16
(7)	$\text{CF}_3\text{H}(\text{g}) + \text{CH}_3(\text{g}) \rightarrow \text{CF}_3(\text{g}) + \text{CH}_4(\text{g})$	0.6 ± 2	17
(37,14,9)	$\text{C}_2\text{F}_6(\text{g}) \rightarrow 2\text{CF}_3(\text{g})$	97.6 ± 6	18

Table V

Deviations of the Observations from the Least Squares Adjustment

<u>i</u>	<u>$R_1 \pm U_1$</u> kcal/gfw	<u>E_1'</u> kcal/gfw	<u>E_1'/U_1</u>
1	157.64 \pm 0.58	0.27	0.47
2	156.22 \pm 1.26	-1.15	-0.91
3	157.18 \pm 1.43	-0.19	-0.13
4	481.89 \pm 1.78	0.15	0.09
5	165.65 \pm 1.04	-0.92	-0.88
6	10.69 \pm 0.70	-0.22	-0.32
7	11.54 \pm 0.32	0.09	0.29
8	25.70 \pm 0.81	-0.10	-0.12
9	14.75 \pm 0.40	0.39	0.98
10	28.02 \pm 0.40	-0.40	-0.99
11	-14.27 \pm 0.50	-0.21	-0.41
12	14.47 \pm 0.50	0.40	0.81
13	53.98 \pm 0.71	-0.18	-0.25
14	54.32 \pm 0.51	0.16	0.31
15	54.70 \pm 3.06	0.54	0.18
16	27.71 \pm 2.00	-0.65	-0.32
17	53.30 \pm 2.01	-0.86	-0.43
18	97.60 \pm 6.00	1.26	0.21
19	84.43 \pm 0.66	0.15	0.23
20	356.69 \pm 2.42	1.37	0.57

(Chi)² = Sum of Squares = 5.70

Birge's Ratio (35) = 0.69

Table VI

Comparison of Selected Values of Enthalpy of Formation

<u>Species</u>	<u>$\Delta H_f^{\circ}_{298.15}$, kcal/gfw</u>		
	<u>This Work</u> <u>(1969)</u>	<u>Lacher(20)</u> <u>(1968)</u>	<u>NBS(38)</u> <u>(1964-66)^a</u>
C ₂ F ₄	-157.4 ± 0.7	-157.4	-155.5
CF ₃	-112.4 ± 1.0	--	-114
CF ₃ H	-166.6 ± 0.8	-166.7 ± 0.7	-164.5
CF ₃ Cl	-169.2 ± 0.8	-169.3 ± 1	-166
CF ₃ Br	-155.1 ± 0.7	-155.0 ± 0.2 -155.2 ± 0.3	-153.6
CF ₃ I	-140.8 ± 0.8	-141.0 ± 0.2	--
CF ₃ CN	-118.4 ± 0.7	--	--
CF ₃ CF ₃	-321.2 ± 1.2	-321.0 ± 1	-310

^aNBS selections (38) were made presumably in the period from about 1964 to 1966.

Table VII

Standard Dissociation Energies of the C-X Bond at 25°C

X =	DH _{298.15} ^o (C-X), kcal/grw					
	H	F	Cl	Br	I	CN
CF ₃ X	106.3±1.3	129.5±0.8	85.8±1.3	69.4±1.2	53.9±1.3	110 ±3
CH ₃ X	104.8±0.2	[109.6±0.8] ^a	84.5±0.3	70.5±0.6	57.0±0.6	117.9±? ^b
Difference	1.5±1.3	[19.9±1.4] ^a	1.3±1.3	-1.1±1.4	-3.1±1.4	-7.9±? ^b
						-4.3±1.6?b

^aBased on an estimated enthalpy of formation for CH₃F (20).^bSome question exists about ΔHf° for CH₃CF₃ (20), while ΔHf° for CH₃CN (34) is based on very old data.

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<p>Status of the JANAF Thermochemical Tables: These now contain 1083 species, including 117 new and 243 revised tables issued during this contract as Supplements 25 through 32. New elements include calcium, cesium and cobalt. The Propellant Ingredient Tables have been issued as a single document combining the final and previous series.</p> <p>Dependencies Among Heats of Formation: The system for keeping track of interrelations and dependencies among species is described.</p> <p>Experimental: Measurements of the low-temperature heat capacity of α-beryllium nitride gave an entropy of 8.157 gibbs/mol at 298°K. Fundamental frequencies of $Al_2Br_6(c)$ were assigned from measurements of infrared spectra.</p> <p>Analysis of Data: Appendices discuss the new JANAF values of ΔH_f° for HF and 13 related fluorides. These values were selected from overdetermined ΔH_f° data using least-squares simultaneous adjustment. Appendix A includes HF, BF₃, CF₄, NF₃ and NaF, while Appendix B includes C₂F₄, CF₃, and CF₃X (X = H, Cl, Br, I, CN, CF₃).</p>		

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	ROLE	WT	ROLE	WT	ROLE	WT
JANAF Thermochemical Table Exhaust Species Propellant Ingredients Simultaneous Adjustment Heat of Formation HF CF ₃ Entropy α -Bc ₃ N ₂ Vibrational Frequencies Al ₂ Br ₃						

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